American Mineralogist, Volume 65, pages 1192-1211, 1980

The high albite–monalbite and analbite–monalbite transitions

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Abstract

The temperatures $T_{\rm diff}$ and $T_{\rm displ}$ of the diffusive transformation high albite–monalbite and the displacive transformation analbite–monalbite were investigated by X-ray powder methods. Alkali feldspars of composition $\rm Or_{0,5,10,20,30}$ were prepared by hydrothermal synthesis at temperatures $T_{\rm equil}$ between 1060 and 700°C. Run durations were sufficiently long (3–72 days) to allow the samples to reach Al,Si equilibrium distributions. $T_{\rm diff}$ can be represented by the equation $T_{\rm diff}[^\circ{\rm C}] = 978 - 19.2 \cdot {\rm Or}$, whereas $T_{\rm displ}$ also depends on $T_{\rm equil}$, *i.e.* the degree of Al,Si order, according to $T_{\rm displ}[^\circ{\rm C}] = 715 - 18.9 \cdot {\rm Or} - 0.221 \cdot {\rm Or}^2 + 0.269 \cdot T_{\rm equil}$. As a consequence $\rm Or_{displ}$, the composition of the triclinic/monoclinic inversion at room temperature, also changes with $T_{\rm equil}$: ${\rm Or_{displ}}[{\rm mol\%}] = 27.5 + 0.00842 \cdot T_{\rm equil}$.

Distinction between topochemically triclinic and monoclinic symmetry is possible on the basis of the temperature variation of lattice angles α, γ and simple line separations; *e.g.* $\cos^2\alpha$ of high albite smoothly approaches but never reaches zero with increasing temperature, whereas $\cos^2\alpha$ of analbite is consistent with a straight-line extrapolation to zero. At room temperature an interval of uncertain distinction extends from $\gamma = 90.18$ to 90.25° and from $\Delta 131 = 1.95$ to 2.00 [°2θ] in high albite and analbite.

Structural explanations are given (1) for the variations of α and γ with Al,Si order in equilibrated albites, (2) for the variations of α and γ due to short-term heating of albite and analbite, (3) for the dependence of $T_{\rm displ}$ and $\rm Or_{displ}$ on $T_{\rm equil}$, (4) for the result $T_{\rm displ} \geq T_{\rm diff}$ in Na-feldspar. $T_{\rm displ}$ is thought to react sensitively on structural disturbances which may be caused by thermal and mechanical history, chemical impurities, and other factors. If $T_{\rm displ}$ is found to be lower than $T_{\rm diff}$, this is ascribed to such defects.

Introduction

The symmetry of Na-rich feldspars in the ternary system $\rm KAlSi_3O_8(Or)$–$\rm NaAlSi_3O_8(Ab)$–$\rm CaAl_2Si_2O_8(An)$ may be either monoclinic or triclinic. This polymorphism is due to two different processes: a *diffusive* and a *displacive* transformation (Laves, 1952a). The extensive literature on this topic up to 1973 has been reviewed by Smith (1974). Since then, emphasis was laid on thermodynamic treatment of the transformations (Thompson *et al.*, 1974; Thompson and Hovis, 1979), on thermal expansion with regard to changes in size and orientation of the thermal expansion ellipsoid (Willaime *et al.*, 1974), on low temperature and high pressure experiments (Grove and Hazen, 1974; Hazen, 1976) and on single-crystal diffractometry to prove or disprove the existence of a monoclinic Na-feldspar at high temperatures (Prewitt *et al.*, 1976; Winter *et al.*, 1978, 1979). In the following the basic features of the polymorphism will be discussed briefly. We will essentially follow the ideas of Laves (1952a,b; 1960), using the concept of an average structure with an ideal C-centered 7Å unit cell (Megaw, 1974, p. 108).

The highest symmetry that a feldspar crystal can possibly attain, when only the three-dimensional configuration of tetrahedral oxygen atoms is considered, is termed *topological* symmetry. It is monoclinic. When the distribution of Al and Si on the tetrahedral sites is accounted for, the symmetry of the idealized framework is called *topochemical* symmetry. This distinction has been introduced by Smith (1970). The following relations between topochemical and actual symmetry are possible in alkali feldspars with the Al:Si ratio 1:3: (a) Disordered alkali feldspars: monoclinic topochemical symmetry ($C2/m$); either monoclinic ($C2/m$) or triclinic ($C\bar{1}$) actual symmetry. (b) Ordered alkali feldspars: triclinic topochemical and thus triclinic actual symmetry ($C\bar{1}$).

Alkaline-earth feldspars with the Al:Si ratio 1:1 are topochemically monoclinic regardless of their Al,Si order.

It is generally accepted that the monoclinic/triclinic symmetry change of Na-rich feldspars is the result of either (1) the *diffusive* transformation, which involves Al,Si order/disorder or (2) the *displacive* transformation, which involves displacement of bond angles.

(1) When a crystal with a disordered, topochemically monoclinic Al,Si distribution is cooled below a critical temperature T_{diff}[1], the Al,Si distribution will become triclinic, provided the cooling is sufficiently slow. The process is reversible and appears to be continuous. In thermodynamic equilibrium the degree of order is a function of the parameters of state, especially of the temperature. Because of the slow transition kinetics, non-equilibria are common.

(2) Without changing the degree of order, triclinic symmetry may be achieved when a topochemically monoclinic crystal is cooled sufficiently rapidly below a critical temperature T_{displ}. The process is reversible, appears to be continuous and proceeds rapidly. Its mechanism is related to the large (A) cations in the interstices of the framework. The topochemical and actual symmetry will both be monoclinic only when the size of the A cation (*e.g.* K) is sufficient to allow contact to all oxygen atoms coordinated in a monoclinic configuration. Otherwise the framework adopts triclinic symmetry by tetrahedral tilting to accommodate the A cation (*e.g.* Na, Ca).

The review articles by Bambauer *et al.* (1974), Ribbe (1975), and Yund (1975) discuss the essential features of the transformations from different points of view, using a nomenclature with partial overlap. To a large extent our study is concerned with the polymorphism in the binary systems Or–Ab and Ab–An in the range $Or_{40}Ab_{60}$–Ab_{100}–$Ab_{80}An_{20}$. The transformation behavior of the mixed crystals is closely related to the polymorphism of Na-feldspar. Based on the pioneering experimental work of MacKenzie (1952, 1957), heating experiments of Schneider (1957),[2] and the theoretical conclusions of Laves (1960) it is generally accepted that there are two *stable* and one *metastable* modifications of Na-feldspars:

(a) Stable modifications

monalbite (Schneider and Laves, 1957): disordered; topochemical and actual symmetry: monoclinic ($C2/m$), corresponding to high sanidine; stable above $T_{\text{diff}} \approx 930$–$980°$ C (range of literature data).

albite: topochemical and actual symmetry: triclinic ($C\bar{1}$); ordered form: low albite, corresponding to low microcline; disordered form: high albite, corresponding to high microcline; stable below T_{diff}.

(b) Metastable modification

If monalbite is rapidly quenched, it undergoes a displacive transformation to triclinic *analbite* ($C\bar{1}$) at $T_{\text{displ}} \approx 930$–$980°$ C (range of literature data). Because analbite is topochemically monoclinic, but metrically triclinic, it is unstable at any temperature. The term "analbite" was chosen by Laves (1952a) following a suggestion of Winchell (1925) based on unequivocal optical data.

Whereas these general relations are accepted, several details are still debated:

(1) How does the Al,Si distribution vary with temperature in stable Na-feldspars? The first diagrammatic representation was given by Hafner and Laves (1957); it was modified by Laves (1960), Stewart and Ribbe (1969), Kroll (1971a,b) and Thompson *et al.* (1974). We do not have sufficient experimental data to decide which might be the correct diagram, especially at temperatures below ~700° C; however, we will see in the last section that we can at least deduce restrictions for the shape of the diagram.

(2) What terminology should we use with disordered Na-feldspars? Some suggestions made by different authors are compiled in Table 1. We will follow the scheme of Laves. It has also been adopted by Raase (1971), Bruno and Pentinghaus (1974), Thompson *et al.* (1974), Waldbaum (1974), Okamura and Ghose (1975), Winter *et al.* (1979), and others. The problem of practical distinction is discussed later.

(3) What is the thermodynamic order of the displacive and diffusive transformation? This question is discussed by Thompson and Waldbaum (1969), Smith (1972; 1974, I, p. 304), Martin

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[1] T_{diff} is equivalent to $T_{\text{M/A}} = T_{\text{Monalbite/Albite}}$ used by Laves (1960) and Thompson *et al.* (1974).

[2] From Schneider's data it can be safely assumed that his samples were not affected by K-contamination from the furnace atmosphere (Brown, 1967).

Table 1. Different terminologies used with disordered Na-feldspars

Topochem./actual symmetry	triclinic/triclinic	monoclinic/triclinic	monoclinic/monoclinic
Laves (1960)	high albite	analbite	monalbite
Smith (1974,I,p.446)	high albite	maximum high albite (inverted monalbite)	maximum high albite (monalbite)
Ribbe (1975, p.R-12)	intermediate albite	high albite (analbite)	high albite (monalbite)
K-feldspar analogon	high microcline	none	high sanidine

(1974), and Bambauer *et al.* (1978). These authors use different types of information: variation of the cell volume due to Na,K substitution (Thompson and Waldbaum), endmember compositions obtained in exsolution experiments (Martin), and variation of cell volume with temperature (Bambauer *et al.*). The latter method will be further pursued in part III of this paper. Closely related is the question of the transition between high albite and low albite (Debron *et al.*, 1968; Raase, 1971) which is even harder to answer, because of the known experimental difficulties in obtaining equilibrium Al,Si distributions. We have not investigated this point.

(4) What are the relations between the temperatures of the diffusive and displacive transformation, T_{diff} and T_{displ}? Using MacKenzie's (1952) data Laves (1960) estimated $T_{\mathrm{diff}} = 980°\mathrm{C}$. He concluded that $T_{\mathrm{displ}} \leq T_{\mathrm{diff}}$. Thompson *et al.* (1974) and Thompson and Hovis (1978) give $T_{\mathrm{diff}} = 965°\mathrm{C}$ and 983°C, respectively, from extrapolations of Grundy and Brown's (1969) data. Kroll and Bambauer (1971) found $T_{\mathrm{displ}} = T_{\mathrm{diff}} = 980°\mathrm{C}$. Detailed discussion is given later.

In the following, the results of Kroll (1971a), Schirmer (1976) and additional investigations on the diffusive and displacive transformation in the feldspar system will be presented. The data are derived from high-temperature X-ray powder photography of equilibrated samples. In this paper we will be concerned with synthetic alkali feldspars in the range $\mathrm{Or_{40}Ab_{60}}$–$\mathrm{Or_0Ab_{100}}$.

Experimental

Sample preparation

The starting material in the hydrothermal syntheses (s.l.) were gels of stoichiometric composition. They were prepared according to a modified version of the method of Luth and Ingamells (1965) using $\mathrm{CaCO_3}$, $\mathrm{K_2CO_3}$, and $\mathrm{C_8H_{20}O_4Si}$ (Merck, p.a.), and Al metal (99.999%) which was kindly provided by the Institut für Metallforschung, Münster. The Ca, K, Na content of the reagents has been determined by titration, the $\mathrm{SiO_2}$ content of the ester by hydrolysis. The An content of the alkali feldspar gels was less than 0.1 wt%.

Charges of ≈200 mg were sealed with small amounts of water in gold capsules (≈0.7 ccm). Bridgman-type autoclaves were used at all temperatures between 700 and 1000°C in run durations between 1700 and 120 h, respectively. According to the experiments of MacKenzie (1952) and Eberhard (1967), these conditions are sufficient to allow the samples to reach steady states with respect to lattice-parameter changes. The steady states probably represent equilibrium Al,Si distributions. Thus we will equate our synthesis temperatures with Al,Si equilibrium temperatures T_{equil}. Above 1000°C experiments could no longer be performed in Bridgman-type autoclaves. We decided to use the method of Greig and Barth (1938). The sample is tightly folded in a platinum foil and sealed in an evacuated tube of silica glass together with a certain amount of $\mathrm{Al(OH)_3}$ separated from the sample. Dehydration of the hydroxide produces a certain water vapor pressure. We usually chose $P(\mathrm{H_2O}) = 5$ bar. As reported by Schirmer (1976), Or-containing samples prepared in this way have lattice constants which are not quite consistent with those derived from samples crystallized in autoclaves. This may be due to some reaction between feldspar and silica glass *via* the water vapor. These samples are not listed in the tables. A corresponding effect was not observed with the $\mathrm{Ab_{100}}$ sample crystallized at 1060°C. However, the Δ111 parameter does not change quite as expected on heating. Samples were usually checked with the polarizing microscope for the presence of phases other than feldspars, with negative results. In Table 2a sample compositions and synthesis conditions are listed. The maximum error of T_{equil} is ±10°C.

X-ray investigation

Lattice parameters measured at room temperature. X-ray powder photographs were taken of all samples at room temperature with an AEG-Guinier-Jagodzinski camera (Cu$K\alpha_1$ radiation). Spec-pure silicon and quartz—both checked against silicon (Parrish, 1960)—were chosen as internal standards. The powder lines were measured with a high-precision ruler and a zoom-binocular (1:10–1:40). The mean error in reading is estimated to be ±0.02 mm $\hat{=}$ 0.01° 2θ. Systematic errors were corrected by a least-squares line or a sequence of straight lines through the standard data points (program JAGOCOR). By comparison with known powder films, 15 to 25 reflections could then be indexed which were used to refine preliminary lattice parameters (program LCLSQ, Burnham, 1962). From these parameters the full powder pattern was calculated (program PUDI, Biedl, 1967) and the indexing was completed. The mean number of reflections used in the final LCLSQ run of triclinic samples was 39. The standard error is mostly ±0.001Å and 0.01°, respectively. From experience we can state that one should not trust in the accuracy of feldspar lattice parameters with *esd*'s of more than 0.003Å and 0.03°. In addition, the number of lines used should not be below 20 in triclinic samples. The room temperature lattice parameters are listed in Table 2a.

Lattice parameters measured at elevated temperatures (25–1050°C). At the beginning of this work no high-temperature powder camera with a satisfactory resolution was commercially available. Therefore,

Table 2a. Composition, conditions of crystallization, and lattice parameters at room temperature of synthetic sodium-rich alkali feldspars

Sample No.	Ab [mol%]	Or [mol%]	T_{equil} [°C]	t [days]	P_{H_2O} [bar]	$T_{X\text{-}ray}$ [°C]	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	V [Å^3]	No. lines
1375 o	100	0	750	70	1000	25	8.152(1)	12.854(1)	7.115(1)	93.67(1)	116.47(1)	89.87(1)	665.7(2)	33
1153	100	0	800	3	1000	25	8.151(1)	12.859(1)	7.114(1)	93.64(1)	116.47(1)	89.97(1)	665.8(1)	59
1306 o	100	0	850	21	700	25	8.152(1)	12.864(1)	7.114(1)	93.60(1)	116.46(1)	90.05(1)	666.2(1)	45
1278 o	100	0	900	11	400	25	8.152(1)	12.867(1)	7.112(1)	93.55(1)	116.45(1)	90.14(1)	666.2(2)	50
1271 o	100	0	950	5	200	25	8.152(1)	12.869(1)	7.111(1)	93.53(1)	116.43(1)	90.21(1)	666.4(1)	53
1291	100	0	1000	4	50	25	8.154(1)	12.869(1)	7.108(1)	93.54(1)	116.44(1)	90.25(1)	666.2(1)	72
1255 m	100	0	1060	8	5	25	8.152(1)	12.870(1)	7.106(1)	93.51(1)	116.43(1)	90.26(1)	665.9(1)	53
1255 u	100	0	1060	21	5	25	8.154(1)	12.872(1)	7.105(1)	93.53(1)	116.42(1)	90.26(1)	666.1(2)	47
1277	100	0	1060	45	5	25	8.156(1)	12.872(1)	7.111(1)	93.47(1)	116.43(1)	90.24(1)	666.9(1)	56
2555 m	95	5	700	48	1	25	8.175(1)	12.879(2)	7.124(1)	93.43(2)	116.45(1)	89.90(2)	670.1(2)	29
2555 o	95	5	750	24	1000	25	8.173(1)	12.867(2)	7.119(1)	93.33(1)	116.44(1)	90.00(1)	668.9(2)	35
2499 m	95	5	800	12	1000	25	8.172(1)	12.874(1)	7.119(1)	93.35(1)	116.46(1)	90.08(1)	669.1(2)	37
2499 o	95	5	850	6	700	25	8.172(1)	12.875(2)	7.118(1)	93.29(1)	116.43(1)	90.19(1)	669.1(2)	50
2461	95	5	900	6	400	25	8.174(1)	12.881(1)	7.118(1)	93.29(1)	116.44(1)	90.23(1)	669.5(1)	36
2493	95	5	950	3	200	25	8.173(1)	12.881(2)	7.119(1)	93.32(1)	116.42(1)	90.24(1)	669.8(2)	35
1375 m	90	10	750	70	1000	25	8.197(1)	12.896(1)	7.130(1)	92.98(1)	116.41(1)	90.15(1)	673.9(2)	31
1337 o	90	10	800	28	1000	25	8.198(1)	12.899(1)	7.129(1)	92.98(1)	116.42(1)	90.21(1)	673.9(1)	43
1306 m	90	10	850	21	700	25	8.196(1)	12.900(1)	7.128(1)	92.99(1)	116.40(1)	90.2[illegible](1)	673.8(1)	41
1278 m	90	10	900	11	400	25	8.197(1)	12.902(1)	7.127(1)	93.02(1)	116.40(1)	90.22(1)	673.8(1)	41
1271 m	90	10	950	5	200	25	8.194(1)	12.901(1)	7.124(1)	93.05(1)	116.41(1)	90.23(1)	673.2(2)	33
1375 u	80	20	750	70	1000	25	8.245(1)	12.930(1)	7.144(1)	92.25(1)	116.35(1)	90.17(1)	681.8(2)	29
1337 m	80	20	800	28	1000	25	8.243(1)	12.932(1)	7.145(1)	92.26(1)	116.35(1)	90.16(1)	681.8(2)	30
1306 u	80	20	850	21	700	25	8.242(1)	12.931(1)	7.139(1)	92.30(1)	116.32(1)	90.17(1)	681.3(2)	41
1278 u	80	20	900	11	400	25	8.239(1)	12.929(1)	7.137(1)	92.34(1)	116.35(1)	90.19(1)	680.5(2)	46
1271 u	80	20	950	5	200	25	8.240(1)	12.931(1)	7.136(1)	92.41(1)	116.35(1)	90.18(1)	680.6(1)	41
1376	70	30	750	70	1000	25	8.286(3)	12.960(3)	7.157(2)	91.20(2)	116.31(2)	90.13(2)	688.8(5)	22
1337 u	70	30	800	28	1000	25	8.28[illegible](2)	12.953(2)	7.155(1)	91.26(2)	116.28(1)	90.10(1)	688.5(3)	20
1309	70	30	850	21	700	25	8.286(1)	12.972(2)	7.153(1)	91.27(1)	116.27(1)	90.10(1)	689.3(2)	25
1280	70	30	900	11	400	25	8.286(1)	12.968(1)	7.151(1)	91.30(1)	116.27(1)	90.11(1)	688.8(2)	24
1273	70	30	950	5	200	25	8.283(2)	12.965(2)	7.152(2)	91.44(2)	116.28(1)	90.12(1)	688.4(4)	16

Kroll (1971a) designed a high-temperature Guinier-Jagodzinski-type camera, a modified version of which was used by Schirmer (1976). Its maximum temperature is 1100°C. The temperature measurement is believed to be accurate within ±5°C. The Pt–PtRh (DIN) thermocouple was calibrated with substances of known melting points used as samples in the camera. Temperature differences within the sample holder are less than 10°C. Contamination of the sample by furnace material can be excluded. Details of construction and efficiency will be reported elsewhere.

The X-ray procedure was as follows. From room temperature the sample temperature was raised stepwise and a powder photograph was taken (~3h) at each step at constant temperature. To detect effects of hysteresis this procedure was also used oscillating, with negative results. After the heating procedure, in some cases a second photograph was taken at room temperature. No changes with respect to the first powder pattern could be detected, which confirms the finding of other authors (*e.g.* Grundy and Brown, 1969) that short-term heating of feldspars does not affect their structural state to any measurable extent.

Calibration of high-temperature diffraction patterns by an internal standard has two disadvantages: (a) the standard may react with the sample, (b) uncertainties in its thermal expansion may cause systematic errors. Following a suggestion by Dr. H. G. Öhlschlegel, Bochum, we used the known room-temperature pattern of the sample itself to correct the high-temperature pattern, both being located on the same film side by side and read off simultaneously. This procedure is time-consuming and its precision may suffer from slight movements of the sample holder during heating. However, the results were superior in precision and consistency to the internal standard method. The quality of a room-temperature pattern taken with the high-temperature camera is not quite as good as that taken with the standard AEG camera, thereby about doubling the error in measurement. The lattice parameters so derived are listed in Table 2b and c.

A different procedure to correct for systematic errors was used with the Ab_{100} samples with numbers H122–H136, where a constant empirical correction factor was assumed. We consider the absolute value of the lattice constants, especially of the cell edges of these samples, to be less trustworthy than those of all the other samples.

Procedures to determine T_{diff} and T_{displ}

To determine the temperature of the diffuse and displacive transformation, T_{diff} and T_{displ}, we have followed the suggestion of Thompson *et al.* (1974) to linearize α (T) by using $\cos^2\alpha$ (T). Extrapolation of $\cos^2\alpha$ to zero indicates the temperature at which high albite and analbite change to monalbite, assuming that α and γ reach 90° at the same temperature, and indicate not only the metrical but also the symmetrical change. Note that expressing $\cos^2\alpha$ as a function of T implies that the corresponding curve α *vs.* T increases to infinity as α reaches 90°. This is not true when α itself rather than $\cos^2\alpha$ is given as a function

Table 2b. Composition, conditions of crystallization, and lattice parameters at equilibrium temperature $T_{equil} = T_{X\text{-}ray}$ of synthetic sodium-rich alkali feldspars

Sample No.	Ab [mol%]	Or	T_{equil} [°C]	t [days.]	P_{H_2O} [bar]	$T_{X\text{-}ray}$ [°C]	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	V [Å^3]	No. lines
HS 11	100	0	750	70	1000	750	8.249(1)	12.949(2)	7.142(1)	92.49(1)	116.20(1)	89.40(1)	683.8(2)	37
HS 12	100	0	850	21	700	850	8.262(1)	12.955(1)	7.151(1)	91.77(1)	116.18(1)	89.86(1)	686.5(1)	30
HS 13	100	0	900	11	400	900	8.273(1)	12.968(1)	7.153(1)	91.41(1)	116.14(1)	89.90(1)	688.7(1)	34
HS 14	100	0	950	5	200	950	8.281(2)	12.982(2)	7.159(1)	90.98(2)	116.12(1)	89.95(2)	690.9(3)	29
HS 15	100	0	1000	4	50	1000	8.287(2)	12.979(2)	7.153(2)	90	116.10(1)	90	690.9(3)	26
HS 16	100	0	1060	8	5	1060	8.301(2)	12.988(2)	7.155(1)	90	116.07(1)	90	692.9(2)	21
HS 17	95	5	700	48	1000	700	8.261(3)	12.933(2)	7.149(1)	92.07(1)	116.27(1)	89.61(1)	684.4(4)	25
HS 18	95	5	750	24	1000	750	8.259(3)	12.931(2)	7.137(2)	91.79(2)	116.28(2)	89.72(2)	683.1(5)	24
HS 20	95	5	800	12	1000	800	8.267(1)	12.935(1)	7.139(1)	91.36(1)	116.18(1)	89.85(1)	684.9(2)	29
HS 21	95	5	850	6	700	850	8.273(2)	12.957(2)	7.149(1)	90.89(2)	116.12(1)	89.96(2)	688.0(3)	28
HS 22	95	5	900	6	400	900	8.285(1)	12.967(2)	7.152(1)	90	116.11(1)	90	689.9(2)	24
HS 23	95	5	950	3	200	950	8.303(1)	12.978(2)	7.155(1)	90	116.06(1)	90	692.6(3)	23
HS 27	90	10	800	88	1000	800	8.290(1)	12.961(2)	7.152(1)	90	116.13(1)	90	690.0(2)	21
HS 28	90	10	850	21	700	850	8.311(3)	12.971(4)	7.148(3)	90	116.09(2)	90	692.1(5)	22
HS 29	90	10	900	11	400	900	8.312(1)	12.969(2)	7.151(1)	90	116.04(1)	90	692.6(2)	27
HS 30	90	10	950	5	200	950	8.316(1)	12.967(2)	7.148(1)	90	116.02(1)	90	692.6(2)	31

Table 2c. Composition, conditions of crystallization, and lattice parameters at temperature $T_{X\text{-ray}}$ of synthetic sodium-rich alkali feldspars

Sample No.	Ab Or [mol%]	T_{equil} [°C]	t [days]	P_{H_2O} [bar]	$T_{X\text{-ray}}$ [°C]	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	V [Å^3]	No. lines
H 129	100 0	950	5	200	509	8.220(3)	12.938(3)	7.134(4)	92.58(2)	116.30(4)	90.12(2)	679.3(8)	18
H 130					761	8.247(4)	12.957(3)	7.141(3)	91.86(3)	116.21(3)	90.07(3)	684.2(7)	19
H 133					985	8.301(2)	12.987(3)	7.153(2)	90.63(2)	116.13(2)	90.03(2)	692.2(4)	24
H 134					1007	8.299(2)	12.983(3)	7.155(2)	90.38(3)	116.04(2)	90.06(1)	692.7(4)	23
H 135					1025	8.307(2)	12.991(3)	7.163(2)	90.29(2)	116.11(2)	90.03(2)	694.1(5)	16
H 136					1057	8.307(3)	12.983(2)	7.152(3)	89.99(2)	116.19(2)	90.01(1)	692.2(5)	17
H 122	100 0	1000	4	50	496	8.218(2)	12.932(2)	7.128(2)	92.65(2)	116.35(1)	90.15(1)	677.9(4)	25
H 123					766	8.253(3)	12.957(2)	7.142(2)	91.77(1)	116.29(2)	90.07(1)	684.3(5)	26
H 124					900	8.273(1)	12.969(2)	7.138(1)	90.98(2)	116.13(1)	90.04(1)	687.5(3)	18
H 127					981	8.299(1)	12.997(1)	7.156(1)	90	116.05(1)	90	693.5(2)	23
H 126					1000	8.307(2)	13.004(2)	7.160(1)	90	116.09(1)	90	694.6(3)	18
1271 u	80 20	950	5	200	20	8.240(1)	12.931(1)	7.136(1)	92.41(1)	116.35(1)	90.18(1)	680.6(1)	41
HS 1					100	8.247(1)	12.940(1)	7.142(1)	92.24(1)	116.29(1)	90.18(1)	682.6(2)	31
HS 2					200	8.258(1)	12.947(1)	7.143(1)	91.92(1)	116.30(1)	90.17(1)	684.2(3)	35
HS 3					300	8.269(2)	12.952(1)	7.143(2)	91.51(2)	116.25(1)	90.12(2)	685.8(4)	29
HS 4					400	8.283(2)	12.973(2)	7.153(1)	91.05(1)	116.20(1)	90.12(1)	689.5(3)	25
HS 5					500	8.309(6)	12.994(5)	7.152(5)	90	116.10(4)	90	693.5(9)	20
HS 6					600	8.323(1)	12.997(1)	7.153(1)	90	116.03(1)	90	695.3(2)	15
HS 7					700	8.336(2)	13.003(1)	7.166(1)	90	116.01(1)	90	698.1(3)	19
HS 8					800	8.364(2)	13.009(2)	7.164(1)	90	115.96(1)	90	700.9(3)	15
HS 9					900	8.387(2)	13.034(2)	7.171(1)	90	115.89(2)	90	705.2(3)	22
HS 10					1000	8.409(2)	13.051(2)	7.188(1)	90	115.83(1)	90	710.0(3)	22

of *T*. The consequences of this point regarding the volume expansion behavior will be discussed in part III of this paper.

A different method to determine T_{diff} and T_{displ} was discussed by MacKenzie (1952) and used by Henderson and Ellis (1976). They follow the temperature variation of the shapes of the merging lines in a powder diffractometer trace and determine that point as transition temperature above which no further change in line shape does occur. This method yields transition temperatures which are higher by up to 100°C than those obtained by methods using line separations. We prefer the $\cos^2\alpha$ method, because it is susceptible to least-squares procedures and its results are dependent only on metrical changes. Recently, Thompson and Hovis (1978) and Hovis (1980) have suggested another parameter showing a linear dependence on temperature: cos ($b\Lambda b^*$). The results are practically the same as those obtained with the $\cos^2\alpha$ method.

Results

Temperature T_{diff} of the diffusive transformation

The temperature at which the reversible change from monoclinic to triclinic topochemistry and symmetry occurs can be found from the variation of lattice angles α and γ. They are plotted for Ab_{100} and Or_5Ab_{95} in Figure 1 as a function of equilibration temperature $T_{equil} = T_{X\text{-ray}}$. The point at which they reach 90° indicates the temperature of the *diffusive* transformation T_{diff}. As the curves are drawn by eye, the estimation of T_{diff} is subjective. It is possible, however, to obtain a higher precision from two other diagrams.

In the first one the lattice angle γ measured at *room* temperature *vs.* the *equilibration* temperature is plotted (Fig. 2). γ is a measure of the difference t_10-t_1m in the Al content of the T_10 and T_1m tetrahedral sites (Stewart and Ribbe, 1969; Kroll, 1973). One would expect a non-zero change of γ with equilibration temperature for topochemically triclinic feldspars and a zero change in case of monoclinic topochemistry. We therefore interpret the steep slopes as representing (K-) high albites and the gentle slopes representing (K-) analbites. Their points of intersection would then correspond to T_{diff}.

This interpretation, however, is not unequivocal. The different slopes could as well represent different dependences of γ (*i.e.* t_10-t_1m) on equilibration temperature in topochemically triclinic samples. We have strong indications for this possibility in Na-rich

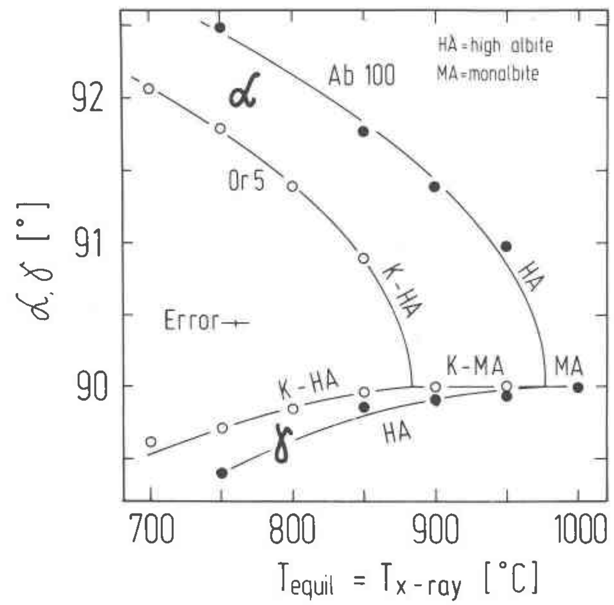

Fig. 1. The variation with equilibrium temperature $T_{\mathrm{equil}} = T_{\mathrm{X\text{-}ray}}$ of the lattice angles α and γ of synthetic alkali feldspars Ab_{100} and Or_5Ab_{95} (data in Table 2b).

plagioclases (Kroll, to be published), but no indications for alkali feldspars including Na-feldspars.

A second possibility to determine T_{diff} was suggested by Thompson *et al.* (1974). Figure 1 shows that α approaches 90° with increasing slope, whereas γ is levelling off. Roughly speaking, α measures the "displacive deviation" of an alkali feldspar from monoclinic symmetry, whereas γ measures the "diffusive deviation." Thus above 700°C the displacive changes in equilibrated albites dominate the diffusive changes, as pointed out by Thompson *et al.* We have used their procedure of plotting $\cos^2\alpha = f(T_{\mathrm{equil}})$ to find T_{diff} for the Ab_{100} and Or_5Ab_{95} samples (Fig. 3). For $Or_{10}Ab_{90}$, T_{diff} cannot be found in this way because the samples have to be equilibrated at temperatures below 700°C, which can hardly be achieved in laboratory times under the chosen experimental conditions. In addition, unmixing at lower temperatures imposes restrictions.

In Table 3 data for T_{diff} given by different authors are listed. The values of Thompson *et al.* (1974) and Thompson and Hovis (1978) were extrapolated from data of Grundy and Brown (1969). We believe that their values and those taken from Figure 3 are the most accurate ones. They agree within the limits of error. From linear extrapolation of T_{diff} (Ab_{100}) = 978°C and T_{diff} (Or_5) = 882°C we find T_{diff} (Or_{10}) = 786°C, in close agreement with the value indicated in Figure 2. Further linear extrapolation to $Or_{\sim 20}$, where T_{diff} would approach the solvus temperature, is justified.

Temperature T_{displ} of the displacive transformation

In principle, monoclinic cell dimensions and symmetry can be achieved only by feldspars which are topochemically monoclinic, as is true for all alkali feldspars equilibrated at $T_{\mathrm{equil}} > T_{\mathrm{diff}}$. It has been shown that samples which on rapid heating reach and stay at a point where α = γ = 90° are also symmetrically monoclinic (Grundy *et al.* 1967; Winter *et al.*, 1979). We will therefore assume that monoclinic cell dimensions imply monoclinic symmetry. Accordingly, Na-feldspars (analbites) which reach α = γ = 90° at elevated temperatures (Figs. 4 and 11) are topochemically monoclinic. Samples for which γ > 90° at room temperature, but γ < 90° at elevated temperatures, cannot be topochemically monoclinic, but are topochemically triclinic high albites.

The distinction between analbite and high albite may be difficult or even impossible using room-temperature lattice parameters (see Prewitt *et al.*, 1976, Table 6); they can be distinguished, however, from their different thermal expansion behavior. It is

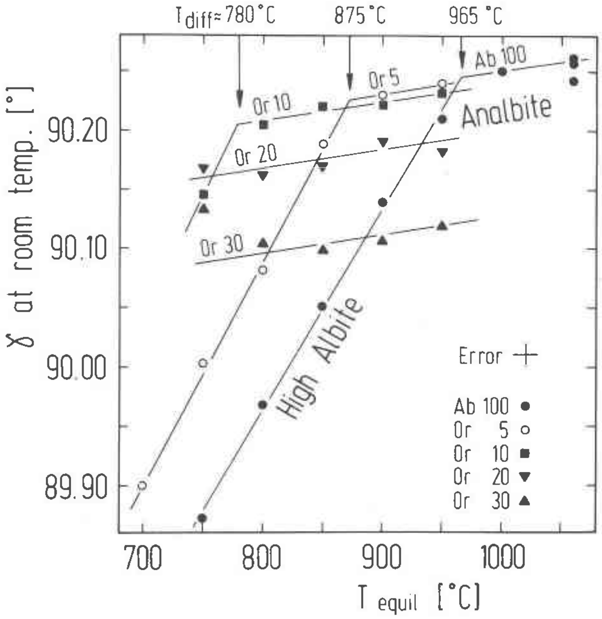

Fig. 2. The lattice angle γ of synthetic alkali feldspars measured at room temperature and plotted as a function of composition and equilibration temperature T_{equil} (data in Table 2a). Arrows point to the intersection of the straight lines which represent (K-) high albites and (K-) analbites. The corresponding temperatures T_{equil} are the temperatures of the diffusive transformation T_{diff}.

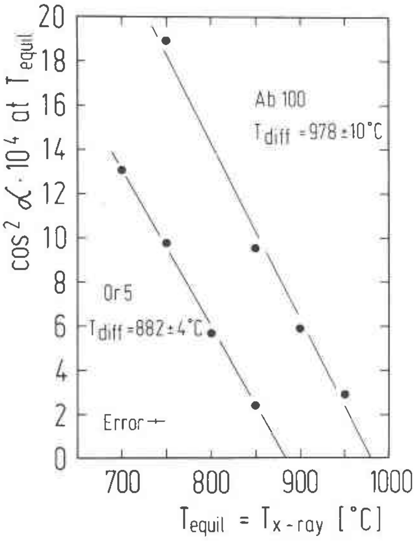

Fig. 3. The variation with equilibrium temperature $T_{equil} = T_{X\text{-}ray}$ of the lattice angle α—plotted as $\cos^2\alpha$—of synthetic alkali feldspars. The regression equations of the straight lines are: Ab_{100}: $\cos^2\alpha \cdot 10^4 = 78.83 - 0.08057 \cdot T_{equil}$; $r^2 = 0.991$; Or_5Ab_{95}: $\cos^2\alpha \cdot 10^4 = 63.54 - 0.07200 \cdot T_{equil}$; $r^2 = 0.998$. T_{diff} corresponds to T_{equil} for $\cos^2\alpha = 0$. *esd*'s given with T_{diff} were derived from a regression of $T_{equil} = f(\cos^2\alpha)$. r^2 = coefficient of determination.

shown schematically in Figures 4 and 11 and has actually been measured by Winter *et al.* (1979) that above about 1000°C the α and γ angles of high albites will follow the temperature axis at a certain distance above (α) and below it (γ), but—in contrast to analbite—will never reach it without further diffusion of Al,Si. The more the samples are ordered, the larger the distance.

The different response of α and γ to rapid heating of an albite sample is puzzling at first sight. Whereas α approaches 90° because the "displacive changes" are removed, the deviation of γ from 90° even increases. Nevertheless, the γ variation, too, is a reflection of the diminishing "displacive changes."

Table 3. Temperatures of the diffusive transformation T_{diff} [°C] of Na-rich alkali feldspars

$Or_{20}Ab_{80}$	$Or_{10}Ab_{90}$	$Or_{05}Ab_{95}$	$Or_{00}Ab_{100}$	
-	-	-	980	Laves (1960)
-	760	-	980	Kroll & Bambauer (1971)
-	-	-	965±5	Thompson et al. (1974)
-	-	-	983	Thompson & Hovis (1978)
-	780	875	965	Fig. 2 of this work
-	-	882±4	978±10	Fig. 3 of this work
594	786	882±4	978±10	Eq. 3

Stewart and von Limbach (1967) were the first to compare the thermal expansion of high and low albite. Grundy and Brown (1969) studied in detail the lattice parameter variation of MacKenzie's (1957) equilibrated albites. They used the reciprocal lattice angles α^* and γ^* of a Na-feldspar synthesized and equilibrated at 1000°C to extrapolate a temperature $T_{X\text{-}ray} = T_{displ} \approx 950$°C, where $\alpha^* = \gamma^* = 90°$. We do

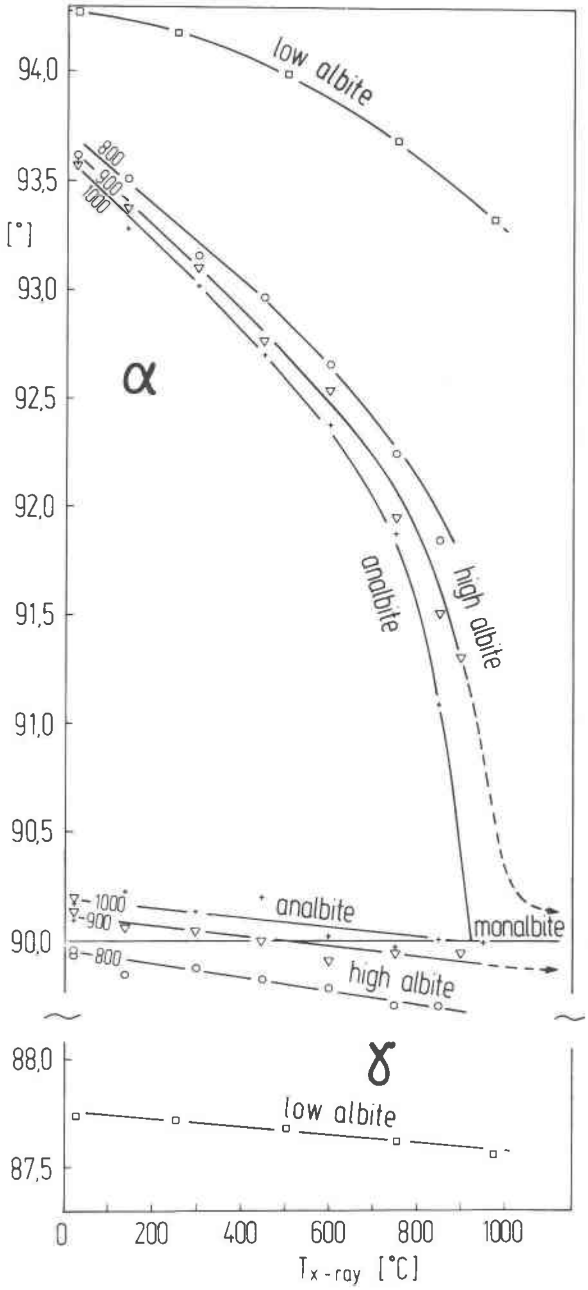

Fig. 4. The variation with temperature $T_{X\text{-}ray}$ of the lattice angles α and γ of low albite and equilibrated synthetic Na-feldspars. The data are taken from Grundy and Brown (1969) and Winter *et al.* (1977). Equilibration temperatures are indicated. Dashed lines show the trend expected for high albites.

not recommend, however, the use of the reciprocal angles. In analbites and high albites both α^* and γ^* are smaller than 90° and increase on heating, such that a formal extrapolation to 90° is possible though meaningless for high albites. α^* and γ^* do not allow, therefore, a clear distinction between high albite and analbite from their temperature variation. By contrast, the γ angle of high albite decreases below 90° on heating, which in itself is an indication of triclinic topochemistry.

A similar warning applies if powder-line separations are to be extrapolated, as can be seen from Figure 5. The line separation $\Delta 111 = 4\theta(111) - 4\theta(1\bar{1}1)$ (Cu$K\alpha_1$) has been plotted *vs.* temperature $T_{\text{X-ray}}$ for $\text{Or}_{0,10,20,30}$ which were equilibrated at various temperatures. To effectively linearize the $\Delta 111$ variation we used $1-\cos^2(\Delta 111)$ in analogy to $\cos^2\alpha$. When the straight lines are extrapolated to zero two situations have to be distinguished:

(a) If alkali feldspars are equilibrated above T_{diff}, *i.e.* if their topochemistry is monoclinic, the extrapolation necessarily yields the temperature of the displacive transformation T_{displ}. Table 5 shows that T_{displ} decreases by about 25°C per 100°C decrease of the equilibration temperature within the monoclinic range. This behavior can be understood from the changes in the oxygen environment of the Na atom which occur on lowering the equilibration temperature. Laves (1960) predicted an opposite dependence of T_{displ} on T_{diff}, whereas Kroll and Bambauer (1971) assumed T_{displ} to be constant.

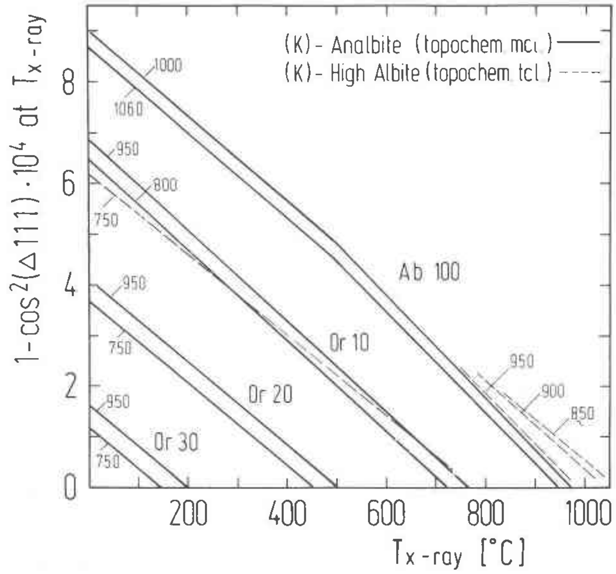

Fig. 5. Temperature variation of the line separation $\Delta 111 = 4\theta(111) - 4\theta(1\bar{1}1)$ (Cu$K\alpha_1$ radiation)—plotted as $1 - \cos^2(\Delta 111)$—for synthetic alkali feldspars, which have been equilibrated at different temperatures T_{equil} between 750 and 1060°C. For the sake of simplicity some straight lines and all data points are omitted. However, all regression equations are given in Table 4. The data are listed by Kroll (1971a).

Table 4. Regression equations $1 - \cos^2(\Delta 111) = a + b \cdot T_{\text{X-ray}} + c \cdot T_{\text{equil}}$ representing the data of Fig. 5 (Kroll, 1971a)

Composition	T_{equil}	$a \cdot 10^4$	$b \cdot 10^6$	$c \cdot 10^2$	r^2	n
Ab_{100}	1000 – 1060°C	15.116	−1.0103	−0.5266	0.999	6
$\text{Or}_{10}\text{Ab}_{90}$	800 – 950°C	4.373	−0.9018	0.2667	0.998	18
$\text{Or}_{20}\text{Ab}_{80}$	750 – 950°C	2.192	−0.8229	0.2042	0.995	21
$\text{Or}_{30}\text{Ab}_{80}$	750 – 950°C	−0.483	−0.8217	0.2221	0.952	11

r^2 : coefficient of determination, n : sample size

(b) If alkali feldspars are equilibrated below T_{diff}, *i.e.* if their topochemistry is triclinic, they cannot undergo a displacive transformation. Hence the extrapolation of $1-\cos^2(\Delta 111)$ or $\cos^2\alpha$ to zero is meaningless in such cases. A discussion of the lattice parameters of Figure 4 shows that, depending on the relative deviations of α and γ from 90°, the value of $\Delta 111$ may even become smaller than zero. Apart from a few known cases (see curves 6,7,8 in Fig. 6), we do not know the temperatures at which α and γ approach a horizontal trend in Figures 4 and 11, which indicates that the displacive part of the "triclinity" is removed and the diffusive part remains. The result of a formal extrapolation to zero has been termed "simulated transformation" by Kroll and Bambauer (1971). The temperatures of these "transformations" increase with decreasing T_{equil} in contrast to the temperatures of the true displacive transformation.[3] It is safe to assume that Na-feldspars for which "transition temperatures" have been extrapolated which are higher than 1000°C or even higher than the melting temperature (1118°C) (*e.g.* Dietz *et al.*, 1970) are topochemically triclinic high albites.

The straight lines in Figure 5 that correspond to case (a) and (b) alkali feldspars, respectively, have different slopes. (K-) analbites are represented by a family of subparallel lines, whereas the (K-) high albite lines have slopes that decrease with decreasing T_{equil} and intersect the parallel lines (*e.g.* Or_{10}, 750°C). Whereas at room temperature $\Delta 111$ has sim-

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[3] This is what Winter *et al.* (1979, p. 422) mean in quoting MacKenzie (1952) and Kroll (1971). Their usage of the term "albite" synonymous with Na-feldspar might also raise confusion.

Table 5. Temperatures of the displacive transformation T_{displ} [°C] of the (K-) analbites of Fig. 5

Composition	T_{equil}	1060	1000	950	900	850	800	750
$Ab_{100}Or_{0}$	T_{displ}	944	975					
$Ab_{90}Or_{10}$	"			766	751	736	722	
$Ab_{80}Or_{20}$	"			502	490	477	465	453
$Ab_{70}Or_{30}$	"			198	185	171	158	144

T_{displ} was calculated from the equations of Table 4.

ilar values in (K-) high albites and (K-) analbites, the variation with temperature is significantly different. An analogous result is obtained when MacKenzie's (1952) data are plotted in the same way.

The variation of $1-\cos^2(\Delta 111)$ in (K-) analbites can be described by equations of the type $1-\cos^2(\Delta 111) = a+b \cdot T_{X\text{-ray}}+c \cdot T_{equil}$ (Table 4). In case of Ab_{100} the straight-line relation is not quite fulfilled in the whole temperature range. We therefore used only data measured at $T_{X\text{-ray}} > 500°C$. It is additionally noticed for Ab_{100} that the straight line for $T_{equil} = 1060°C$ is displaced to lower values of $T_{X\text{-ray}}$ relative to the 1000°C line, which is in contrast to the uniform trend seen with the Or-containing samples. We already mentioned in "Experimental" that samples prepared by the Greig and Barth method tend to have lattice parameters which are not quite consistent with those derived from samples prepared in autoclaves, the reasons for which are not known to us. The effect is only barely visible in Ab_{100} crystallized at 1060°C: α (93.47°) and $\Delta 131$ (1.965°) appear to be slightly low, and correspondingly T_{displ} is low. Whatsoever, it appears that small changes in lattice parameters of topochemically monoclinic crystals have a pronounced effect on T_{displ}.

For a further comparison of high albites and analbites we will discuss the temperature variation of the lattice angle α—plotted as $\cos^2\alpha$—of Na-feldspars prepared at temperatures $>T_{diff}$, either by direct synthesis or by dry heat-treatment of low and intermediate albites (Fig. 6). Two types of curves can be distinguished: (a) those which can be linearly extrapolated to a well-defined transition temperature T_{displ} at $\cos^2\alpha = 0$: curves (3), (4), (5); (b) those which do not intersect, but approach the abscissa at high temperatures: curves (6), (7), (8). Their slopes are not as steep as those of the type (a) curves, although all $\cos^2\alpha$ values are similar at room temperature, a situation analogous to Figure 5.

We interpret the type (a) curves to represent analbites which transform to monalbites at T_{displ}, whereas the type (b) curves represent high albites which cannot undergo a displacive transformation at any temperature. The samples represented by curves (6) and (7) have been dry heat-treated at temperatures well above T_{diff}. However, the annealing was apparently not sufficient to produce equilibrium, *i.e.* a topochemically monoclinic Al,Si distribution. This interpretation is also given by Winter *et al.* (1979) for their heat-treated Tiburon sample (curve 7).

The linear extrapolation of the type (a) curves is justified from curve (5): two powder diagrams taken just above (981°C) and below (960°C) the transformation temperature (968°C), which was extrapolated from the data points at 496, 766 and 900°C, indicate monoclinic and triclinic symmetry, respectively. The photograph taken at 960°C shows broadened lines whose separations, however, could not be measured. This data point is therefore not plotted in Figure 6. Although we do not expect it, we cannot completely exclude the possibility that the (a) curves slightly

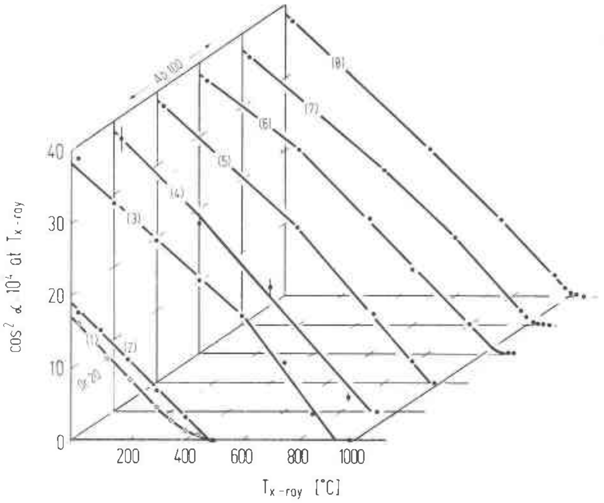

Fig. 6. Temperature variation of the lattice angle α—plotted as $\cos^2\alpha$—for Na-feldspars, which have been either directly synthesized or dry heat-treated at temperatures $>T_{diff}$. Two $Ab_{80}Or_{20}$ samples are plotted for comparison. Note that for all data points of curves (6) to (8) it is $\cos^2\alpha > 0$, whereas for curves (1) to (5) $\cos^2\alpha = 0$ at the highest temperature. Sources of data: (1) Henderson and Ellis (1976): synthetic K-analbite $Or_{20}Ab_{80}$ (700°C, 6–10 d, 1 kbar). (2) This work: synthetic K-analbite $Or_{20}Ab_{80}$ (950°C, 5 d, 0.2 kbar). (3) Grundy and Brown (1969): synthetic analbite Ab_{100} (1000°C, 6 d, 2000 psi). (4) Okamura and Ghose (1975): low albite (Amelia) (annealed at 1080°C, 133 d). (5) This work: synthetic analbite Ab_{100} (1000°C, 4 d, 0.05 kbar). (6) Prewitt *et al.* (1976): synthetic intermediate albite (annealed at 1060°C, 40 d). (7) Winter *et al.* (1979): low albite (Tiburon) (annealed at 1080°C, 60 d). (8) This work: synthetic high albite (950°C, 5 d, 0.2 kbar).

bend over near T_{displ}, similar to the (b) curves. This effect, however, would be comparatively small and could not be resolved by standard methods.

Prewitt *et al.* (1976) point out that even very precise film methods are inferior to a single-crystal diffractometer if small line separations are to be measured. This is certainly true. Nevertheless, the precision of the Guinier-Jagodzinski method used by us is sufficient to detect the different thermal variations of the α angles in Na-feldspars crystallized at 1000°C and 950°C, *i.e.* only 25°C above and below T_{diff}, respectively (curves 5 and 8).

The change in slope of the (b) curves near $\cos^2\alpha = 0$ can be interpreted like the trend of α and γ given schematically in Figures 4 and 11 at high temperatures: it corresponds to the thermal expansion of high microcline, because at temperatures above ~1000°C the displacive changes in the high albite structure are more or less absent.

The type (a) curves are not linear over the whole temperature range. It appears justified, however, to assume a linear variation within a limited range. We have used the last three data points for a regression line. T_{displ} obtained in this way is listed in Table 6. Note that the value of $T_{displ} = 968$°C calculated from $\cos^2\alpha$ agrees within limits of error with $T_{displ} = 975$°C calculated from $\cos^2(\Delta\ 111)$. Comments on the large temperature range displayed in Table 6 are given later (Tables 4 and 5).

Curve (1) and (2) are similar in appearance to type (b) and (a) curves, respectively, although both of the Or_{20} samples are K-analbites, because they have been prepared at temperatures $>T_{diff}$. However, when the solvus is approached, chemical fluctuations are to be expected. These would cause the slope of the $\cos^2\alpha$ curve to decrease at high temperatures, because Na-rich regions would dominate in a sample with a Na-rich bulk composition. The curve (1) sample has been prepared at 700°C (Henderson and Ellis, 1976), the curve (2) sample at 950°C (Kroll, 1971a). Henderson and Ellis give $T_{displ} = 560$°C for their sample, and suspect that 500°C given by Kroll (1971a) for his sample may be low, because line separations like $\Delta 111$ used by Kroll will be underestimated when the lines are less than ~0.15°2θ apart. This argument, repeated in Henderson (1979), simply does not apply, as Kroll only used $\Delta 111$ when the separation was larger than ~0.15°2θ. Rather, it appears that Henderson and Ellis' estimate of T_{displ} is high, because their synthesis temperature was low.

Table 6. Temperatures of the displacive transformation T_{displ} [°C] of the analbites of Fig. 6

Curve	T_{displ}	References
(3)	928 ± 25	Grundy & Brown (1969)
(4)	903 ± 36	Okamura & Ghose (1975)
(5)	968 ± 8	this work

To further rationalize the difference in T_{displ} Henderson incorrectly quotes Bambauer *et al.* (1978), saying that "the temperatures of the monoclinic/triclinic inversion *decreases* with increasing temperature." However, Figure 5 shows that T_{displ} *decreases* with *decreasing* T_{equil} ($T_{equil} > T_{diff}$), which is in accordance with Bambauer *et al.*

As a consequence, the composition at which the monoclinic/triclinic symmetry change occurs at room temperature (abbreviated as Or_{displ}) will decrease in Or content when T_{equil} is decreased (Fig. 7). The straight lines purposely cover only that compositional range in which the Al,Si distribution is topochemically monoclinic, as judged from the known T_{diff}. From a comparison of Figures 6 and 7, it appears that the variations of $\cos^2\alpha$ with chemical composition follow a linear relation more closely than does the temperature variation.

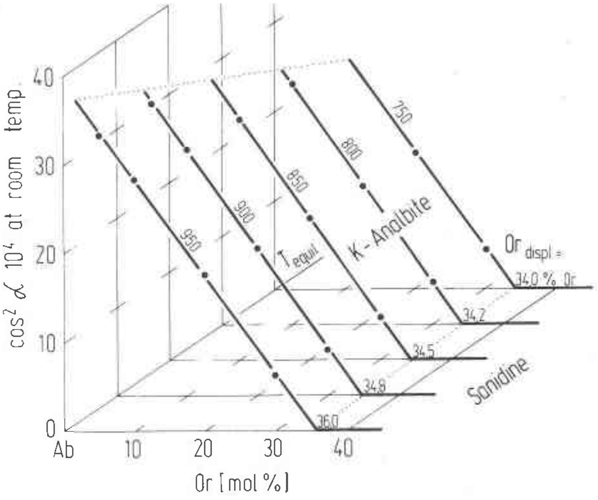

Fig. 7. Relation between the lattice angle α—measured at room temperature and plotted as $\cos^2\alpha$—and Or content of K-analbites, which have been equilibrated at T_{equil} = 750–950°C. Extrapolation to $\cos^2\alpha = 0$ yields the composition at which the monoclinic/triclinic change occurs at room temperature (Or_{displ}). Values of Or_{displ} as indicated in the figure were calculated from the individual straight-line regression equations. The total of the $\cos^2\alpha$ data can be represented by the equation $\cos^2\alpha \cdot 10^4 = 30.4 - 1.104 \cdot Or + 0.0093 \cdot T_{equil}$, where Or is mol% K-feldspar. The coefficient of determination is $r^2 = 0.9994$. From this equation the variation of Or_{displ} with T_{equil} is found to be $Or_{displ} = 27.5 + 0.0084 \cdot T_{equil}$.

In a thorough study of all published data, Hovis (1980) independently reached the same conclusion as Bambauer *et al.* (1978) with regard to the dependence of $\mathrm{Or}_{\mathrm{displ}}$ on T_{diff}. Since Hovis discusses the literature on this controversial subject, we will not pursue this point further. It suffices to say that the dependence, which Hovis and we find, means that $\mathrm{Or}_{\mathrm{displ}}$ is slightly dependent on the Al,Si order in a topochemically monoclinic sample. This was first pointed out in an abstract by Waldbaum (1974). The structural explanation will be given later in the discussion.

Our results on T_{diff} and T_{displ} of Na-rich alkali feldspars are summarized in Figure 8, which shows the relation between the stable phase boundary of the *diffusive* transformation high albite–monalbite and the metastable phase boundaries of the *displacive* transformation analbite–monalbite. For the sake of simplicity only three curves of the displacive transformation are given: for samples equilibrated at 800, 1000, and 1100°C.

The transition temperatures given in Table 5 can be reproduced by an equation of the form $T_{\mathrm{displ}} = \mathrm{a} + \mathrm{b}{\cdot}\mathrm{n}_{\mathrm{Or}} + \mathrm{c}{\cdot}\mathrm{n}_{\mathrm{Or}}^2 + {\cdot}T_{\mathrm{equil}}$, from which the curves representing $T_{\mathrm{equil}} = 1000$ and 1100°C were calculated in Figure 8. As in Figure 7, only those data points must be used to draw the curve for $T_{\mathrm{equil}} = 800$°C which correspond to topochemically monoclinic samples.

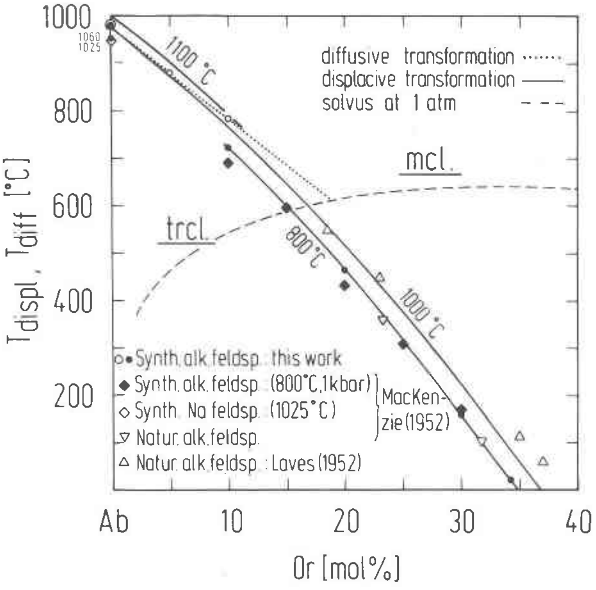

Fig. 8. Stable phase boundary of the diffusive transformation high albite ⇄ monalbite (·······) and metastable phase boundaries of the displacive transformation analbite ⇄ monalbite (———) of Na-rich alkali feldspars for $T_{\mathrm{equil}} = 800°, 1000°, 1100°\mathrm{C}$. Temperatures T_{diff} as given in text, data for T_{displ} as listed in Table 5. The variation of T_{displ} is given by the regression equation $T_{\mathrm{displ}} = 715 - 18.9 \cdot \mathrm{Or} - 0.221 \cdot \mathrm{Or}^2 + 0.269 \cdot T_{\mathrm{equil}}$, where Or is mol% K-feldspar. The coefficient of determination is $r^2 = 0.9995$. The temperature of the diffusive transformation follows a straight line: $T_{\mathrm{diff}} = 978 - 19.2$ Or, which meets the 1-atm solvus of Thompson and Waldbaum (1969) at ~600°C and $\mathrm{Or}_{\sim 20}$.

For a comparison, transformation temperatures for MacKenzie's (1952) samples equilibrated at 800°C have been extrapolated in exactly the same way as the data in Figure 5, omitting topochemically triclinic samples. The results agree excellently with our 800°C curve. In addition, data points of some natural alkali feldspars with a small An content have been plotted. They were obtained by Laves (1952b) by measuring extinction angles on a microscope heating stage, and by MacKenzie (1952) who used a powder diffractometer. Because of lack of data, the transformation temperatures could not be extrapolated after linearizing the curves as in Figure 5, and they are therefore not quite comparable to the points in Figure 8. Nevertheless, the position of MacKenzie's samples, which is close to the 800°C curve, appears to be reasonable. It might thus be promising to investigate the cooling history of analbite phases in anorthoclases by a comparison with the curves of Figure 8. Other transformation temperatures given in the literature, which most probably correspond to "simulated transformations," are not plotted. See Smith (1974, I, p. 301–305) for a full summary.

Neglecting literature data, we now have three different temperatures T_{displ} for Ab_{100} equilibrated at 1000°C: 984°C from the equation of Figure 8, 975°C derived from $1 - \cos^2(\Delta 111)$, and 968°C from $\cos^2\alpha$. We would get still another T_{displ} using Thompson and Hovis' (1978) parameter $1 - \cos(b\Lambda b^*)$. Although we consider all of them identical within the limits of error, we favor the value of 984°C, as it is based on the largest number of data points.

Two more temperatures T_{displ} are plotted in Figure 8 for Na-feldspars equilibrated at 1060 and 1025°C, which against our expectation fall below the data point for $T_{\mathrm{equil}} = 1000$°C. However, as already discussed in connection with the 1060°C sample, T_{displ} is very sensitive to any changes in the experimental conditions. Therefore, both the 1060° and 1025°C sample cannot be strictly compared to all the other samples. This is also true for the analbites of Grundy and Brown (1969) and Okamura and Ghose (1975); see Figure 6, curves (3) and (4), and Table 6. T_{displ} of the sample of Grundy and Brown is 928±25°C. Thompson *et al.* (1974) and Thompson and Hovis (1979) determined T_{diff} to be 965° and 983°C, respectively. Thus the analbite of Grundy and Brown behaves analogously to our 1060°C sample. The sensitivity of T_{displ} is not unexpected, if we assume that the displacive transformation is not a first-order transition (see part III of this paper). An analogous argument applies to T_{diff}.

Summary of the results on T_{displ}, $\mathrm{Or}_{\mathrm{displ}}$, and T_{diff}

The data on T_{displ} were derived from the variation of Δ111 with temperature (Fig. 5, Table 5) and the variation of α with Or content (Fig. 7: $T_{\mathrm{displ}} = 25°\mathrm{C}$ at $\mathrm{Or}_{\mathrm{displ}}$). They can be summarized by the equation:

$$T_{\mathrm{displ}}[°\mathrm{C}] = 715 - 18.9 \cdot \mathrm{Or} - 0.221 \cdot \mathrm{Or}^2 + 0.269 \cdot T_{\mathrm{equil}} \qquad (1)$$

From the room-temperature variation of $\cos^2\alpha$ with Or content (caption to Fig. 7) the dependence of $\mathrm{Or}_{\mathrm{displ}}$ on T_{equil} is found to be:

$$\mathrm{Or}_{\mathrm{displ}}[\mathrm{mol\%}] = 27.5 + 0.00842 \cdot T_{\mathrm{equil}} \qquad (2)$$

The dependence of T_{diff} on Or content can be derived from the variation of $\cos^2\alpha$ with T_{equil} in high albites of composition Ab_{100} and Or_5 (Fig. 3):

$$T_{\mathrm{diff}}[°\mathrm{C}] = 978 - 19.2 \cdot \mathrm{Or} \qquad (3)$$

The dependence of T_{displ} and $\mathrm{Or}_{\mathrm{displ}}$ on T_{equil} implies a dependence on the Al,Si distribution. When the variation of Al site occupancies of the topochemically monoclinic samples in Table 2a is investigated by the *b,c* method of Stewart and Ribbe (1969) or the 110 method of Kroll (1980), it is found that the Al content of the T_1 tetrahedral sites $\mathrm{t}_1\mathrm{0} + \mathrm{t}_1\mathrm{m}$ increases by only 0.025–0.055, when T_{equil} is lowered from 950 to 750°C. The corresponding decrease of T_{displ} and $\mathrm{Or}_{\mathrm{displ}}$ by ~55°C and ~2 mol%, respectively, reflects these site-occupancy changes.

It follows from equation 1 that for pure Na-feldspar T_{displ} decreases from 1016° to 978°C when T_{equil} is lowered from 1118° (melting temperature) to 978°C. For all temperatures below 978°C T_{equil} would be lower than T_{displ}, *i.e.* samples equilibrated at such temperatures would be metrically triclinic and consequently they would develop a topochemically triclinic Al,Si distribution. Therefore, $T_{\mathrm{equil}} = T_{\mathrm{displ}} = 978°\mathrm{C}$ is the temperature of the diffusive transformation of Na-feldspar. This result agrees with $T_{\mathrm{diff}} = 978°\mathrm{C}$ found from equation 3, which was derived from a completely different set of information.

The temperatures $T_{\mathrm{equil}} = T_{\mathrm{displ}}$ for Or_5 are found to be 841° and 689°C, respectively. However, their respective temperatures T_{diff} are higher by $\Delta T = 41°$ and 97°C. When these ΔT values, including ΔT(Na-feldspar) = 0°C, are extrapolated by a second-order polynomial to Or_{20} (which admittedly is daring), ΔT is found to be 254°C. As $T_{\mathrm{equil}} = T_{\mathrm{displ}}$ is 340°C for Or_{20}, its T_{diff} would be 594°C, in agreement with $T_{\mathrm{diff}} = 594°\mathrm{C}$ resulting from equation 3. The numerical identity happens by chance, of course. Anyway, we think that we can draw with some confidence the phase boundary for the diffusive transformation as a straight line between 978° at Ab_{100} to 549°C at Or_{20}, where it dips below the 1-atm solvus of Thompson and Waldbaum (1969); see Figure 8.

Discussion

We will now be concerned with the structural reasons for the variation of the lattice angles α and γ with Al,Si distribution, temperature, and chemical composition, with the relation of T_{displ} and $\mathrm{Or}_{\mathrm{displ}}$ to T_{equil} and T_{diff}, and with the practical distinction between analbite and high albite. However, before going into the structural details we will reevaluate our point of view regarding the one- and two-step ordering behavior of the alkali feldspars as mentioned in the introduction.

One-step–two-step ordering

The relative variation with temperature of the Al content in the non-equivalent tetrahedral sites of Na-feldspar can usefully be discussed with reference to a plot of the lattice parameters b *vs.* γ, first introduced by Müller (1970) as b^* *vs.* γ^*. Their variation is given in Figure 9 for Na-feldspars of various structural states. Natural and synthetic samples follow a straight line directly connecting analbite to low albite ("Direktweg" of Kroll, 1971a, 1973; corresponding to "one-step trend" of Smith, 1970; 1974, I, p. 60). Na-feldspars prepared from K-feldspars by Na-exchange follow a detour ("Umweg"—"two-step trend"), the upper part of which corresponds to topochemically monoclinic Al,Si distributions, inherited from the parent K-feldspars; the lower part represents triclinic distributions. We will now discuss the meaning of "one-" and "two-step trend" in terms of tetrahedral site occupancies.

The b parameter is a measure of the sum $\mathrm{t}_1\mathrm{0}+\mathrm{t}_1\mathrm{m}$ of the Al content in the $\mathrm{T}_1\mathrm{0}$ and $\mathrm{T}_1\mathrm{m}$ tetrahedra, whereas γ measures the difference $\mathrm{t}_1\mathrm{0}-\mathrm{t}_1\mathrm{m}$ (Stewart and Ribbe, 1969; Kroll and Ribbe, 1980). In Na-feldspars the variation of b with $\mathrm{t}_1\mathrm{0}+\mathrm{t}_1\mathrm{m}$ and of γ with $\mathrm{t}_1\mathrm{0}-\mathrm{t}_1\mathrm{m}$ is linear. As a consequence, the one-step line in Figure 9 represents a linear relation between $\mathrm{t}_1\mathrm{0}+\mathrm{t}_1\mathrm{m}$ and $\mathrm{t}_1\mathrm{0}-\mathrm{t}_1\mathrm{m}$, which implies that $\mathrm{t}_1\mathrm{0}$ and $\mathrm{t}_1\mathrm{m}$

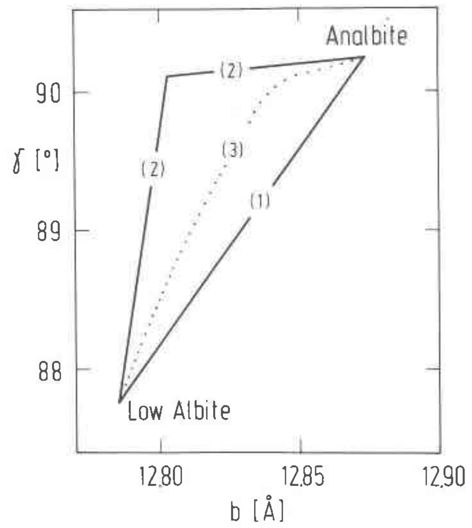

Fig. 9. Room temperature variation of b with γ in Na-feldspars. (1) One-step trend followed by Na-feldspars which were originally grown as Na-feldspars. (2) Two-step trend followed by Na-feldspars which were prepared from K-feldspars by K-exchange techniques. (3) Hypothetical ordering path. Data for curves (1) and (2) are given by Kroll (1971a, 1973).

themselves vary linearly according to $t_10 = 1-3 \cdot t_1m$. From $t_10+t_1m + t_20+t_2m = 1$, it follows that $3 \cdot t_1m = t_1m+t_20+t_2m$ and $t_1m = t_20 = t_2m$, with the understanding that the sign of equality does not hold strictly, because the tetrahedra are crystallographically and thus energetically different. The result $t_10 > t_1m = t_20 = t_2m$ has been confirmed by a structure analysis of a natural intermediate albite $Ab_{84.5}Or_{7.5}An_8$ with mean tetrahedral distances $\langle T_10\text{–}O\rangle = 1.670Å$, $\langle T_1m\text{–}O\rangle = 1.637Å$, $\langle T_20\text{–}O\rangle = 1.638Å$, $\langle T_2m\text{–}O\rangle = 1.637Å$ (Kroll, 1978).

In their analysis of the temperature variation of the tetrahedral Al content, Laves (1960, Fig. 7) and Thompson *et al.* (1974, Fig. 13) deduced that within a large temperature range $t_10 > t_1m > t_20 = t_2m$. The discussion given above does not support this type of variation, but reaffirms the result of Stewart and Ribbe (1969, Fig. 6) and Kroll (1971b, Fig. 1) that $t_1m = t_20 = t_2m$. In the b, γ plot the lattice parameter variation corresponding to the trends given by Laves and Thompson *et al.* would principally follow a curve intermediate between the one- and two-step trend (dotted curve), thereby resembling a two-step behavior in the triclinic region. For a final decision, however, a high-temperature structure refinement of a high albite performed at T_{equil} would be necessary.

In accordance with Smith (1974, I, p. 60) we define the ideal one-step trend as characterized by Al,Si distributions such that $1 \geq t_10 \geq t_1m = t_20 = t_2m \geq 0$, with the meaning of the sign of equality as mentioned above. However, as there is a temperature range of about 140°C where monoclinic monalbite exists and where t_1 and t_2 diverge with decreasing temperature, Na-feldspars only approximately follow the ideal one-step trend.

The ideal two-step trend is defined by Al,Si distributions such that $0.5 \geq t_1 \geq t_2 \geq 0$ and $1 \geq t_10 > t_1m \geq t_20 = t_2m \geq 0$ in the monoclinic and triclinic range, respectively, subject to the constraints $t_1+t_2 = 0.5$ and $t_10+t_1m+t_20+t_2m = 1$. As K-feldspars probably do not reach a state where $t_1 = 0.5$ and $t_2 = 0$ (for a conflicting view see Prince *et al.*, 1973), they only approximate the ideal two-step trend.

We purposely do not speculate on any effects arising from fine-scale domain textures, but refer to the overall pattern as reflected by light optical and standard powder and single-crystal methods. Electron microscopy may bring some contrast into the gray overall pattern, so that we can better understand the small-scale processes of ordering.

"Diffusive changes" of the α and γ angles due to ordering at constant temperature

We follow Thompson *et al.* (1974) and subdivide the deviation of α and γ from 90° into two portions related to the "displacive" and "diffusive" departure of the structure from monoclinic symmetry. If a feldspar is annealed at a constant temperature below T_{diff}, its lattice angle change at this temperature represents the diffusive portion.

As shown by Kroll (1971a, 1973) the diffusive variation of γ is best explained in terms of changes in length of the [110] and [1$\bar{1}$0] diagonals in the (001) plane. The sequence of tetrahedra in [110] is T_10, T_20, T_2m, in [1$\bar{1}$0] it is T_1m, T_20, T_2m, *i.e.* T_10 tetrahedra into which the larger Al atoms concentrate during ordering only occur along [110]. As a consequence, the [110] repeat increases and the [1$\bar{1}$0] repeat decreases during ordering, which means that γ becomes smaller. The absolute change is about the same in Na- and K-feldspar and amounts to ~2.5°.

The reason for the diffusive variation of α can be found from a discussion of the changes in the environment of the A cation. We will consider the sanidine → microcline transition, because it is free from displacive changes (Fig. 10). In the (100) plane the K cation is surrounded by 4 tetrahedra: two T_10 and two T_1m tetrahedra. During ordering Al migrates from T_1m into T_10. As a consequence, the oxygen atoms coordinated to Al become underbonded in

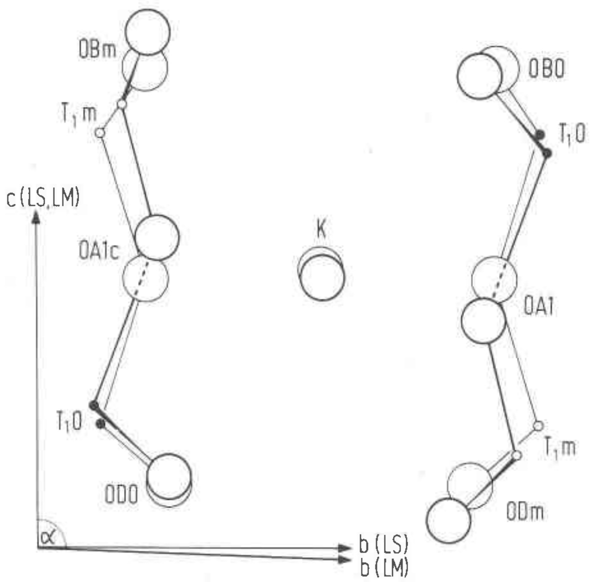

Fig. 10. Projection onto the (100) plane of the oxygen environment of K in low sanidine (LS) and low microcline (LM). For clarity, the atomic and angular shifts from LS to LM have been exaggerated by a factor of 3. OC and OA2 oxygen atoms are not shown. Light circles: LS, heavy circles: LM.

electrostatic terms, and those coordinated to Si become overbonded. For compensation the OB0 and OD0 atoms move towards the K atom, whereas the OBm and ODm atoms enlarge their distance to K (Table 7). As the OB0 . . . OD0 vector is roughly parallel to [011] and the OBm . . . ODm vector parallel to [0$\bar{1}$1], the [011] repeat decreases and simultaneously the [0$\bar{1}$1] repeat increases. Consequently the angle α widens during ordering. The absolute changes are 0.65° and 0.74° for the sanidine → microcline and analbite → low albite transitions, respectively, when measured at room temperature. They are much smaller than the changes in γ. This is to be expected because the necessary K–O readjustments are small compared to the combined effect of the changes of the T–O distances in the [110] and [1$\bar{1}$0] diagonals.

Table 7. Distances [Å] between potassium and its oxygen neighbors in a plane about parallel (100) in low sanidine (LS) and low microcline (LM) (Fig. 10)

	LS	LM	References
d(K-OB0)	3.045	2.961	LS:
d(K-OBm)	3.045	3.136	Colville & Ribbe (1968)
d(K-OD0)	2.945	2.892	LM:
d(K-ODm)	2.945	2.993	Brown & Bailey (1964)

As a consequence of the A–O distance variation, the OB0 . . . OBm and OD0 . . . ODm vectors rotate clockwise. An even larger rotation is found with the OA1 . . . OA1 vector, which is caused by the increasing $T_1$0–OA1 and decreasing T_1m–OA1 distances. This is not true for all feldspars: for example, when boron is substituted for aluminum as in reedmergnerite, the T–OA1 changes are reversed and the OA1 . . . OA1 vector rotates counterclockwise and compensates the clockwise rotation of the OB . . . OB and OD . . . OD vectors. We would therefore expect that the α angle is about the same in the ordered and disordered forms of reedmergnerite, and indeed we find the difference to be only 0.1° (Bruno and Pentinghaus, 1974, Table 7).

A discussion of the α angle variation is also given by Blasi (1978). However, we reject his explanation for reasons which will be given by Kroll in *Tschermaks Mineralogisch-Petrographische Mitteilungen.*

"Displacive changes" of the α and γ angles due to short-term heating at constant Al,Si order

If a topochemically and metrically monoclinic Na-feldspar is rapidly cooled below T_{displ}, its α and γ angles increase from 90° to 93.5 and 90.3° respectively at room temperatures (Fig. 4). These changes are purely displacive in nature, as the Al,Si order is unaffected. The structural reason for this α variation is again found in the oxygen environment of the Na atom in the (100) plane (compare Fig. 10). When the thermal vibration of the Na atom becomes too small with decreasing temperature to hold open the rectangular oxygen array, it collapses to an approximate parallelogram, which causes α to deviate from 90°.[4] This explanation was given independently by Megaw (1974), Bruno and Facchinelli (1974), and is nicely illustrated by Ribbe (1975, Fig. R-9).

The concomitant change in γ is small (~0.25°), because no plane of Na-coordinating oxygen atoms, whose configuration might change, occurs in the (001) plane. It is always found in topochemically monoclinic but metrically triclinic feldspars (*e.g.* analbite, anorthite) that α and γ are both > 90°. Kroll and Müller (1980) give an explanation in terms of volume changes: when α becomes > 90° the cell volume decreases, other things being equal. A simultaneous decrease in γ would counteract the decrease in volume. An increase in γ, however, would support

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[4] This idea was first drawn to the attention of one of us (H.U.B.) by F. Laves in his lecture on feldspars held at Zürich in the winter term of 1963/4.

it. Obviously this is the choice the crystal makes in deciding in what direction γ should change. We thus consider its variation as a side effect of the primary necessity of Na to adjust in its oxygen environment on cooling.

In an albite crystal, the total deviation of α and γ from 90° is due to diffusive and displacive changes. The displacive changes are removed on short-term heating. Hence we expect α to decrease with temperature, and from the interpretation of the change of γ as a side effect of the change of α we also expect γ to decrease (Fig. 4). A closer look into the structure reveals that the temperature variation of γ can be related to the T–O–T angle variation within the tetrahedral chains along [110] and [1$\bar{1}$0]. Angles at 0-oxygen atoms occur only in [110], angles at m-oxygen atoms only in [1$\bar{1}$0]. Table 8 shows that in low albite and analbite as judged from high albite[5] the angles at OBm, OCm are both larger than those at OB0, OC0. On heating, the "0-angles" increase, the "m-angles" decrease. Thus the [110] repeat will increase, the [1$\bar{1}$0] repeat will decrease, and consequently γ will become smaller. The increasing similarity between T–O–T angles at 0- and m-oxygen atoms is the result of the overall tendency of the crystal to approach monoclinic symmetry on heating. The variation of γ from 90° in albites is an apparently contradictory consequence of this tendency. Besides T–O–T angles, other factors such as tetrahedral tilting and Na–O interactions will play a rôle in the variation of γ. We have depicted the T–O–T angles, because their relation to γ is easily visualized.

Table 8. Temperature variation of T–O–T angles centered at the pseudomirror-related oxygen atoms in the [110] and [1$\bar{1}$0] chains of T and O atoms

T-O-T	HA(25°C)	MA(980°C)	LA(25°C)	LA(970°C)
OB0	141.4°	151.2°	139.7°	143.9°
OBm	158.8	151.2	160.9	159.4
OC0	130.4	133.6	129.6	130.7
OCm	134.6	133.6	136.0	135.2

References:
HA: Winter et al. (1979)
MA: Winter et al. (1979)
LA (25°C): Wainwright (in Smith, 1974)
LA (970°C): Winter et al. (1977)
HA = high albite, MA = monalbite, LA = low albite

In Figure 11 we summarize the three possible and principally different changes of α and γ with temperature in Na-feldspars:

(a) *α,γ variation in analbite due to rapid heating.* The size of α and γ is solely determined by the displacive changes, which decrease with increasing temperature to become zero, when analbite inverts to monalbite at T_{displ}, where $\alpha = \gamma = 90°$.

(b) *α,γ variation with equilibrium temperature $T_{equil} = T_{X\text{-}ray}$ in equilibrated albites.* The size of α and γ in albites depends on displacive as well as diffusive changes. In Figure 11 the diffusive influence at an arbitrary temperature is marked by heavy arrows. Light arrows show the influence of the displacive changes. γ is almost completely dependent on diffusive changes, whereas α is dominated by displacive changes. Both are acting in the same direction in the case of α, tending to increase it, but work in opposite directions in the case of γ. At $T_{equil} = T_{diff}$ the α and γ angles reach 90° and high albite inverts to monalbite.

(c) *α,γ variation in albite due to rapid heating.* Only the displacive part of the "triclinicity" decreases on rapid heating. The remaining diffusive portion prevents α and γ reaching 90°. This becomes immediately evident from a comparison of high albite at high temperatures with high microcline at room temperature. The α and γ angles of both feldspars slightly deviate from 90°, α being larger, γ smaller than 90°, because the diffusive changes tend to in-

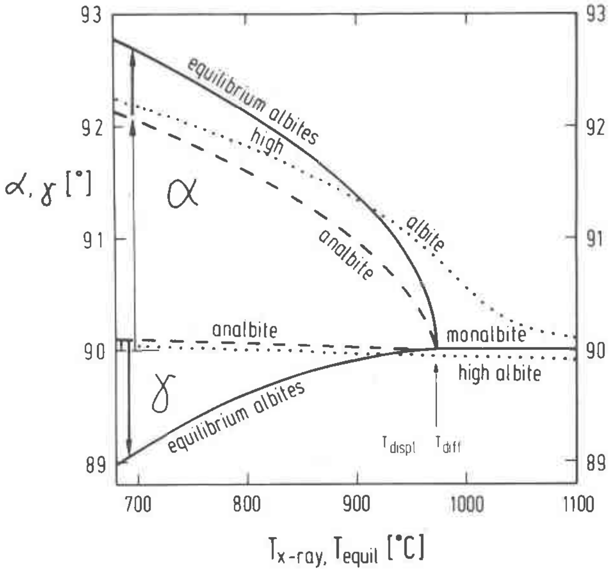

Fig. 11. Variation of α and γ with temperature (a) when analbite and high albite are rapidly heated, (b) when Na-feldspars are heated through Al,Si equilibrium states. For further explanations see text.

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[5] A room-temperature structure refinement of a Na-feldspar known to be analbite is not available in the literature.

crease α and decrease γ by mechanisms which were explained above.

Influence of K-substitution on α and γ

Entrance of K into the Na-feldspar structure reduces the displacive part of the "triclinicity," leaving the diffusive portion constant, a behavior which is similar (though not identical) to an increase in temperature. As a consequence, α and γ both become smaller in the analbite–high sanidine series with progressive K-substitution (Donnay and Donnay, 1952; Laves, 1952b) to reach $\alpha = \gamma = 90°$ at $Or_{\sim 36}$.

In the metastable low alkali feldspar series (Orville, 1967) γ also becomes smaller between Or_0 (87.7°) and $Or_{\sim 40}$ (87.6°), because the displacive changes are successively removed, and then starts to increase and reaches 87.7° in microcline and 88.05° in Rb-microcline (Bruno and Pentinghaus, 1974). From this behavior we would expect γ to increase slightly when microcline is heated, in accordance with the results of Henderson (1979).

The α angle decreases rapidly in the low series between Or_0 (94.1°) and $Or_{\sim 40}$ (91.8°), which is also due to the decreasing displacive changes, and then levels off towards Or_{100} (90.65°). It reaches 90.51° in Rb-microcline (Bruno and Pentinghaus, 1974). The measurements of Henderson (1979) confirm the expectation that the change of α is very small when microcline is heated.

The change in γ due to substitution of the alkali cation is considerably smaller than the change in α, in analogy to a variation in temperature. This is merely another consequence of the fact that changes of γ are mainly diffusive, those of α mainly displacive in nature.

T_{displ}: its relation to T_{equil} and T_{diff}

From a comparison of the variation of Al site occupancies with temperature in K- and Na-feldspar (Fig. 5 of Laves, 1960, in Smith, 1974, I, p. 423, and Fig. 2 of Kroll, 1971b), it can be seen that the topology of both "ordering diagrams" is similar below the microcline/sanidine and low albite/high albite transitions. The main difference is the occurrence of the high albite region between low albite and monalbite at about the same temperatures where sanidine is found in the K-feldspar diagram. The reason is obviously found in the "effective size" of the Na atom, which is too small at the low to high albite transition to expand a (potentially) topochemically monoclinic framework to monoclinic geometry. Hence a triclinic Al,Si distribution is retained, because in a triclinic cell the four symmetrically non-equivalent tetrahedral sites are energetically different and are thus occupied by Al in different amounts. Controlled by the size of the Na atom, which is effectively growing with increasing equilibrium temperature, the Al,Si distribution becomes increasingly disordered, until at $T_{diff} = 978°C$ the Na atom is large enough to expand a framework to monoclinic geometry, which at the same point is allowed by the same reason to become topochemically monoclinic. We exclude the possibility that a stable analbite might exist at temperatures $T > T_{diff}$, *i.e.* we assume that in equilibrium with temperature triclinic geometry and monoclinic topochemistry are mutually exclusive in alkali feldspars. This does not affect the possibility that analbite may be found metastable at $T > T_{diff}$.

Figure 8 shows that T_{displ} varies directly with T_{equil}: the lower T_{equil}, the lower T_{displ}. The reason is found from a discussion of structural variations: in a topochemically monoclinic feldspar Al migrates at equal rates from T_2 into T_1 tetrahedra as the equilibration temperature is decreased. The OA1 oxygen atoms bridging two T_1 tetrahedra become successively underbonded, while the OA2 atoms located between two T_2 tetrahedra become overbonded. For compensation the A–OA1 distances decrease, whereas the A–OA2 distances increase, as seen with the unheated and heated sanidine crystals of Weitz (1972). The A atoms, which are situated slightly above the plane of OB,OD atoms (Fig. 10), move closer to the plane. Consequently, in case of (K-) monalbite a quench to (K-) analbite will result in an α angle which becomes smaller the closer the Na atom approaches the OB,OD plane, *i.e.* the more ordered the (K-) monalbite is. As a side effect γ will also decrease, but to a lesser extent. This behavior is nicely seen with the Or_{20} and Or_{30} samples (Table 2a), which were equilibrated between 950° and 750°C as topochemically monoclinic feldspars.

The smaller the room-temperature deviation of α and γ from 90° in such a sample, the lower will be the temperature T_{displ} and the lesser the Or content of Or_{displ} necessary to reach monoclinic symmetry. The observed decrease of T_{displ} and Or_{displ} with T_{equil} is thus a consequence of the movement of the Na,K atom towards the center of the plane of OB,OD oxygen atoms, with increasing Al occupancy of the T_1 tetrahedra.

Based on this reasoning, we will discuss the relation between T_{diff} and T_{displ}. Figure 8 shows that monalbite equilibrated at 1100°C would invert to analbite at $T > T_{diff}$, whereas K-monalbite with Or > 12 mol% would invert to K-analbite at $T < T_{diff}$. It follows from the mere existence of the displacive transformation that the ability of Na to expand a topochemically monoclinic framework to monoclinic geometry (its "effective size") is greater than necessary at $T > T_{displ}$ and smaller at $T < T_{displ}$, as schematically shown in Figure 12. As explained above, the distance of Na to the OB,OD plane is expected to become larger on disordering of monalbite. On quenching through the monoclinic region, at each temperature this distance would be greater than on cooling through equilibrium stages. Hence the "size" of Na necessary for expansion has to be greater in non-equilibrated than in equilibrated Al,Si distributions. It will follow a curve (2) not as steep as the equilibrium curve (1) and will therefore meet the "potential size" curve (3) at $T_{displ} > T_{diff}$. Figure 12 also shows that T_{displ} decreases with T_{equil}, until at the intersection point of the two curves $T_{equil} = T_{displ} = T_{diff}$. From this consideration we would expect that in pure Na-feldspar the monalbite → analbite inversion would occur always at $T_{displ} > T_{diff}$, in agreement with the results derived from the equation given in Figure 8. This might clarify the statements given by Smith (1974, I, p. 301).

When analbite is held at temperatures $T < T_{diff}$ it changes to albite; when it is held at $T > T_{diff}$, it will change to monalbite by rearrangement of its topochemically monoclinic Al,Si distribution and by movement of Na towards the OB,OD plane, so that Na regains its ability to expand the framework.

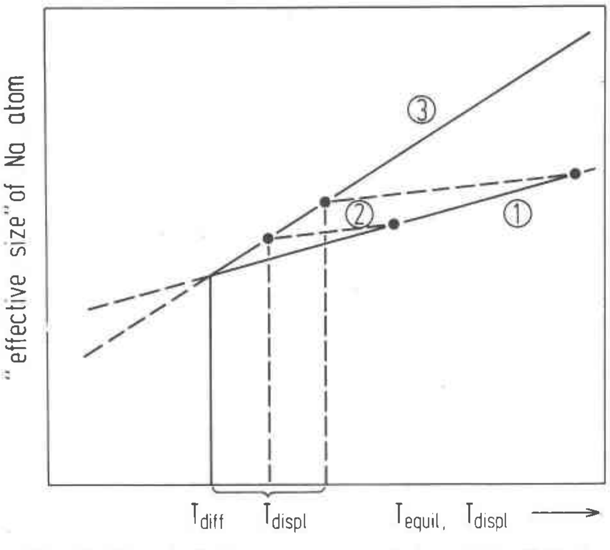

Fig. 12. Hypothetical temperature variation of the "effective size" of the Na atom. Curves (1) and (2): Na "size" necessary to expand a topochemically monoclinic framework to monoclinic geometry, if the Al,Si distribution is in equilibrium (curve 1) or non-equilibrium (curves 2) with temperature. Curve (3): "potential Na size", comparable to the "no-rattle" limit (Bloss, 1971, p. 234).

The reasoning from which we expect that in Na-feldspars $T_{displ} \geq T_{diff}$ should also apply to Or-containing alkali feldspars. However, we observe that with increasing Or content, T_{displ} becomes increasingly lower than T_{diff} (Fig. 8); for example, a sample of Or_{10} prepared just above $T_{diff} = 786°C$ would displacively become monoclinic at ~725°C. The same sample quenched to, say, 750°C would still be monoclinic; however, on further annealing, it would diffusively become triclinic, even though the average effective size of the Na,K atom should be sufficient to ensure monoclinic cell dimensions. The explanation may be that within the Na,K fluctuations in the mixed crystal, Na-rich regions dominate and might initiate the development of triclinic topochemistry at temperature $T_{diff} > T_{displ}$.

Practical distinction between high albite and analbite

Inspection of Figure 2 would suggest that at least the γ angle is suitable for a distinction between high albite and analbite. We think that this is true only if a series of Na-feldspars is prepared from the same starting material using the same experimental procedure, and if the lattice constants are determined using the same X-ray and data processing techniques. Any deviation from these conditions may lead to an overlap of analbite and high albite room-temperature lattice parameters, as was demonstrated by Prewitt *et al.* (1976). However, if for a given Na-feldspar crystal γ is found to be $\geq 90.25°$ or $\Delta 131 = 2\theta(131) - 2\theta(1\bar{3}1)$ ($CuK\alpha_1$) to be $\geq 2.00°$, we expect this crystal to be analbite. Similarly, if $\gamma \leq 90.18°$ or $\Delta 131 \leq 1.95$ one probably deals with high albite. Data that fall in between these values do not allow a distinction. We therefore suggest that any previously proposed values of γ and $\Delta 131$ assumed to uniquely separate high albite from analbite be abandoned. The possibilities and fallacies in distinguishing from high-temperature data are discussed previously. Optical data such as the optic axial angle $2V_x$ provide another means of distinction. $2V_x = 48°$ is the approximate upper value for analbite, whereas high albite may also have smaller values of $2V_x$, due to fine-scale twinning (Kroll, 1971a; Stewart, 1974; Tröger, 1979, p. 126).

In cases where high albite and analbite cannot be distinguished, we suggest the term "highly disordered Na-feldspar" to express the ambiguity. Such pure Na-feldspars are usually prepared artificially; because of their K content, the natural feldspars are usually micro- to crypto-antiperthitic, and in addition micro- to cryptotwinned. If it is not clear whether K-analbite, K-high albite, Na-sanidine, *etc.*, are present within the morphological unit, we suggest the term "anorthoclase" (Bambauer, 1963) be used.

Acknowledgments

We are indebted to the late Professor Dr. F. Laves, whose ideas were basic for our understanding of the alkali feldspar polymorphism. He was closely associated with us during the early stages of this work. We thank Drs. S. Ghose, G. L. Hovis, and C. T. Prewitt for critically reading the manuscript. Special thanks are due to G. L. Hovis for friendly and informative cooperation. The technical assistance of Ms. G. v. Cölln and Mrs. I. Schmiemann in data collecting and preparation of tables and drawings is gratefully acknowledged.

References

Bambauer, H. U. (1963) Feldspat-Familie. In W. E. Tröger, *Optische Bestimmung der gesteinsbildenden Minerale, Teil 2,* p. 645–752. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.

———, H. Kroll and U. Schirmer (1978) Phase transformation and thermal expansion of synthetic, sodium-rich alkali feldspars (abstr.). *Phys. Chem. Minerals, 3,* 57.

———, ———, H. E. Nager and H. Pentinghaus (1974) Feldspat-Mischkristalle—eine Übersicht. *Bull. Soc. fr. Minéral. Cristallogr., 97,* 313–345.

Biedl, A. (1967) *Programm zur Berechnung des Pulverdiagramms aus Gitterkonstanten.* Inst. Mineral., Ruhr-Univ., Bochum.

Blasi, A. (1978) Structural explanation for $\Delta(\alpha^*\gamma^*)$ from α^* *vs.* γ^* in alkali feldspar. *Tschermaks Mineral. Petrogr. Mitt., 25,* 47–56.

Bloss, F. D. (1971) *Crystallography and Crystal Chemistry.* Holt, Rinehart and Winston, New York.

Brown, B. E. and S. W. Bailey (1964) The structure of maximum microcline. *Acta Crystallogr., 17,* 1391–1400.

Brown, W. L. (1967) A reinterpretation of monalbite. *Mineral. Mag., 36,* 80–82.

Bruno, E. and A. Facchinelli (1974) Correlations between the unit cell dimensions and the chemical and structural parameters in plagioclase and alkaline-earth feldspars. *Bull. Soc. fr. Minéral. Cristallogr., 97,* 378–385.

——— and H. Pentinghaus (1974) Substitution of cations in natural and synthetic feldspars. In W. S. MacKenzie and J. Zussman, Eds., *The Feldspars,* p. 574–609. Manchester University Press, Manchester, England.

Burnham, C. W. (1962) IBM computer program for least-squares refinement of crystallographic lattice constants. *Carnegie Inst. Wash. Year Book, 61,* 132–135. Adapted by A. Biedl to the IBM system 360/50.

Colville, A. A. and P. H. Ribbe (1968) The crystal structure of an adularia and refinement of the structure of orthoclase. *Am. Mineral., 53,* 25–27.

Debron, G., J. Wyart and G. Sabatier (1968) Quelques observations sur la transformation hydrothermale de l'albite basse-température en albite haute-température. *C.R. Acad. Sci. Paris, 267* (D), 1345–1350.

Dietz, E. D., T. Baak and H. H. Blau (1970) The superheating of an albite feldspar. *Z. Kristallogr., 132,* 340–360.

Donnay, G. and J. D. H. Donnay (1952) The symmetry change in the high-temperature alkali feldspar series. *Am. J. Sci., Bowen Vol., 250A,* 115–132.

Eberhard, E. (1967) Zur Synthese der Plagioklase. *Schweiz. Mineral. Petrogr. Mitt., 47,* 385–398.

Greig, J. W. and T. F. W. Barth (1938) The system $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ (nephelite, carnegieite)–$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$ (albite). *Am. J. Sci., 35,* 93–112.

Grove, T. L. and R. M. Hazen (1974) Alkali feldspar unit-cell parameters at liquid nitrogen temperatures: low temperature limits of the displacive transformation. *Am. Mineral., 59,* 1327–1329.

Grundy, H. D. and W. L. Brown (1969) A high-temperature X-ray study of the equilibrium forms of albite. *Mineral. Mag., 37,* 156–172.

———, ——— and W. S. MacKenzie (1967) On the existence of monoclinic $NaAlSi_3O_8$ at elevated temperature. *Mineral. Mag., 36,* 83–88.

Hafner, S. and F. Laves (1957) Ordnung/Unordnung und Ultrarotabsorption II. Variation der Lage und Intensität einiger Absorptionen von Feldspäten. Zur Struktur von Orthoklas und Adular. *Z. Kristallogr., 109,* 204–225.

Hazen, R. M. (1976) Sanidine: predicted and observed monoclinic to triclinic reversible transformations at high pressure. *Science, 194,* 105–107.

Henderson, C. M. B. (1979) An elevated temperature X-ray study of synthetic disordered Na–K alkali feldspars. *Contrib. Mineral. Petrol., 70,* 71–79.

——— and J. Ellis (1976) Thermal expansions of synthetic alkali feldspars. In G. M. Biggar, Ed., *Progress in Experimental Petrology,* p. 55–59. National Environment Research Council, London.

Hovis, G. L. (1980) Angular relations of alkali feldspar series and the triclinic–monoclinic displacive transformation. *Am. Mineral., 65,* 770–778.

Kroll, H. (1971a) *Feldspäte im System* $NaAlSi_3O_8$–$KAlSi_3O_8$–$CaAl_2Si_2O_8$*: Al,Si-Verteilung und Gitterparameter, Phasen-Transformationen und Chemismus.* Inaug.-Diss. der Westf. Wilhelms-Universität, Münster.

——— (1971b) Determination of Al,Si distribution of feldspars from X-ray powder data. *Neues Jahrb. Mineral. Monatsh.*, 91–94.

——— (1973) Estimation of the Al,Si distribution of feldspars from the lattice translations Tr[110] and Tr[1$\bar{1}$0]. I. Alkali feldspars. *Contrib. Mineral. Petrol., 39,* 141–156.

——— (1978) The structure of heat-treated plagioclases An28,An52, An69 and the estimation of Al,Si order from lattice parameters (abstr.). *Phys. Chem. Minerals, 3,* 76–77.

——— (1980) Estimation of the Al,Si distribution of alkali feldspars from lattice translations tr[110] and tr[1$\bar{1}$0]. Revised diagrams. *Neues Jahrb. Mineral. Monatsh*, 31–36.

——— and H. U. Bambauer (1971) The displacive transformation of (K,Na,Ca)-feldspars. *Neues Jahrb. Mineral. Monatsh.,* 413–416.

——— and W. F. Müller (1980) X-ray and electron optical investigation of synthetic high-temperature plagioclases. *Phys. Chem. Minerals, 5,* 255–277.

——— and P. H. Ribbe (1980) Determinative diagrams for Al,Si order in plagioclases. *Am. Mineral., 65,* 449–457.

Laves, F. (1952a) Phase relations of the alkali feldspars. I. Introductory remarks. *J. Geol., 60,* 436–460.

——— (1952b) Phase relations of the alkali feldspars. II. The stable and pseudo-stable phase relations in the alkali feldspar system. *J. Geol., 60,* 549–574.

——— (1960) Al/Si-Verteilungen, Phasen-Transformationen und Namen der Alkalifeldspäte. *Z. Kristallogr., 113,* 265–296.

Luth, W. C. and C. O. Ingamells (1965) Gel preparation of starting materials for hydrothermal experimentation. *Am. Mineral., 50,* 255–258.

MacKenzie, W. S. (1952) The effect of temperature on the symmetry of high-temperature soda-rich feldspars. *Am. J. Sci., Bowen Vol., 250A,* 319–342.

——— (1957) The crystalline modifications of $NaAlSi_3O_8$. *Am. J. Sci., 255,* 481–516.

Martin, R. F. (1974) Controls of ordering and subsolidus phase relations in the alkali feldspars. In W. S. MacKenzie and J. Zussman, Eds., *The Feldspars,* p. 313–339. Manchester University Press, Manchester, England.

Megaw, H. D. (1974) Tilts and tetrahedra in feldspars. In W. S. MacKenzie and J. Zussman, Eds., *The Feldspars,* p. 87–113. Manchester University Press, Manchester, England.

Müller, G. (1970) Der Ordnungs-Unordnungs-Übergang in getemperten Mikroklinen und Albiten. *Z. Kristallogr., 132,* 212–227.

Okamura, F. P. and S. Ghose (1975) Analbite → monalbite transition in a heat-treated twinned Amelia albite. *Contrib. Mineral. Petrol., 50,* 211–216.

Orville, P. M. (1967) Unit-cell parameters of the microcline–low albite and the sanidine–high albite solid solution series. *Am. Mineral., 52,* 55–86.

Parrish, W. (1960) Results of the I.U.Cr. precision lattice parameter project. *Acta Crystallogr., 13,* 838–850.

Prewitt, C. T., S. Sueno and J. J. Papike (1976) The crystal structures of high albite and monalbite at high temperatures. *Am. Mineral., 61,* 1213–1225.

Prince, E., G. Donnay and R. F. Martin (1973) Neutron diffraction refinement of an ordered orthoclase structure. *Am. Mineral., 58,* 500–507.

Raase, P. (1971) Zur Synthese und Stabilität der Albit-Modifikationen. *Tschermaks Mineral. Petrogr. Mitt., 16,* 136–155.

Ribbe, P. H. (1975) The chemistry, structure and nomenclature of feldspars. In P. H. Ribbe, Ed., *Feldspar Mineralogy,* p. R1–R51. Mineral. Soc. Am. Short Course Notes, Vol. 2.

Schirmer, U. (1976) *Die Ordnungen der Diffusiven und der Displaziven Umwandlung bei Na-reichen Alkalifeldspäten.* Diplom-Arbeit, Universität Münster.

Schneider, T. R. (1957) Röntgenographische und optische Untersuchung der Umwandlung Albit–Analbit–Monalbit. *Z. Kristallogr., 109,* 245–271.

——— and F. Laves (1957) Barbierit oder Monalbit? *Z. Kristallogr., 109,* 241–244.

Smith, J. V. (1970) Physical properties of order–disorder structures with special reference to feldspar minerals. *Lithos, 3,* 145–160.

——— (1972) Critical review of synthesis and occurrence of plagioclase feldspars and a possible phase diagram. *J. Geol., 80,* 505–525.

——— (1974) *Feldspar Minerals.* I. *Crystal Structure and Physical Properties.* II. *Chemical and Textural Properties.* Springer-Verlag, Heidelberg.

Stewart, D. B. (1974) Optic axial angle and extinction angles of alkali feldspars related by cell parameters to Al/Si order and composition. In W. S. MacKenzie and J. Zussman, Eds., *The Feldspars,* p. 145–161. Manchester University Press, Manchester, England.

——— and D. von Limbach (1967) Thermal expansion of low and high albite. *Am. Mineral., 52,* 389–413.

——— and P. H. Ribbe (1969) Structural explanation for variations in cell parameters of alkali feldspar with Al,Si-ordering. *Am. J. Sci., 267A,* 444–462.

Thompson, J. B. and G. L. Hovis (1978) Triclinic feldspars: angular relations and the representation of feldspar series. *Am. Mineral., 63,* 981–990.

——— and ——— (1979) Structural-thermodynamic relations of the alkali feldspars. *Proc. Am. Crystallogr. Assoc.,* in press.

——— and D. R. Waldbaum (1969) Mixing properties of sanidine crystalline solutions. III. Calculations based on two-phase data. *Am. Mineral., 54,* 811–838.

———, ——— and G. L. Hovis (1974) Thermodynamic properties related to ordering in end-member alkali feldspars. In W. S. MacKenzie and J. Zussman, Eds., *The Feldspars,* p. 218–248. Manchester University Press, Manchester, England.

Tröger, E. (1979) *Optical Determination of Rock-forming Minerals, Part 1, Determinative Tables.* Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.

Waldbaum, D. R. (1974) Critical behavior of the displacive monoclinic–triclinic symmetry change in $NaAlSi_3O_8$–$KAlSi_3O_8$ crystalline solutions (abstr.). *Bull. Soc. fr. Minéral. Cristallogr., 97,* 345.

Weitz, G. (1972) Die Struktur des Sanidins bei verschiedenen Ordnungsgraden. *Z. Kristallogr., 136,* 418–426.

Willaime, C., W. L. Brown and M. C. Perucaud (1974) On the orientation of the thermal and compositional strain ellipsoids in feldspars. *Am. Mineral., 59,* 457–464.

Winchell, A. N. (1925) Studies in the feldspar group. *J. Geol., 33,* 714–727.

Winter, J. K., S. Ghose and F. P. Okamura (1977) A high-temperature study of the thermal expansion and the anisotropy of the sodium atom in low albite. *Am. Mineral., 62,* 921–931.

———, F. P. Okamura and S. Ghose (1978) An investigation of the analbite to monalbite transition and the crystal structure of monalbite at 980 and 1060° C (abstr.). *Phys. Chem. Minerals, 4,* 101–103.

———, ——— and ——— (1979) A high-temperature structural study of high albite, monalbite, and the analbite–monalbite phase transition. *Am. Mineral., 64,* 409–423.

Yund, R. A. (1975) Subsolidus phase relations in the alkali feldspars with emphasis on coherent phases. In P. H. Ribbe, Ed., *Feldspar Mineralogy,* p. Y1–Y24. Mineral. Soc. Am., Short Course Notes, Vol. 2.

Manuscript received, July 17, 1979;
accepted for publication, March 4, 1980.